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Operational extractives management from mountain pine beetle-attacked lodgepole pine for pulp and papermaking

Larry Allen and Vic Uloth

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Abstract

This report addresses the impact of mountain pine beetle infestation on extractives in pulp and paper mills and their impact on process operation. The main concerns addressed include: extractives in pulp, pitch control, friction properties of paper, effluent treatment, and soap separation in the kraft chemical recovery system. In kraft mills, use of beetle-affected wood in the green and red stages did not cause a change in the normal amount of extractives across the mill (after unbleached washing) that is greater than the normal variability. For gray-stage wood, however, preliminary results suggest that the amount of extractives in the final pulp can be significantly higher. Because of the higher resin acid content of beetle-affected wood in green and red stages, good brownstock washing is especially important in kraft mills. High resin acid content in the wood results in an increased solubility of fatty and resin acids in black liquor and a decrease in soap recovery to zero in kraft mills using gray-stage wood. Use of beetle-affected wood in thermo-mechanical pulping (TMP) pulp and paper mills did not seem to cause significant changes in the normal amounts of extractives and their chemical composition across the mill. Use of a pitch dispersant for pulping of green- and red-stage beetle-affected wood to prevent plugging of grooves in refiner plates may be necessary. The friction properties of newsprint made from beetle-affected wood were within the normal range for newsprint. Effluent treatment plants in TMP pulp and paper mills successfully reduced the extractives of effluents during use of beetle-affected wood to near-zero values. In the kraft mill using gray stage infested wood, the resin acid concentration in the final effluent was high.

Keywords: Mountain pine beetle, lodgepole pine, wood extractives, extractives, pitch, fatty acids, resin acids, sterols, sterol esters, triglycerides, pitch control, pulp and paper processing, kraft mills, TMP, paper mills, effluent management, soap, soap recovery, tall oil, friction, paper friction, coefficient of friction

Résumé

Le présent rapport porte sur l'incidence de l'infestation du dendroctone du pin ponderosa sur les matières extractibles du bois dans les usines de pâtes et papiers et son incidence sur le fonctionnement du processus de fabrication. Les principales préoccupations soulevées dans le présent document comprennent : les matières extractibles dans la pâte, le contrôle de la poix, les propriétés de friction du papier, le traitement des effluents, et la séparation du savon dans la récupération des produits chimiques du processus kraft. Dans les usines de pâtes kraft, l'utilisation du bois infesté aux stades vert et rouge n'a pas provoqué de changement dans la quantité normale de matières extractibles dans l'usine (après lavage de la pâte écrue) supérieur à la variabilité habituelle. Cependant, dans le cas du bois au stade gris, les résultats préliminaires laissent entendre que la quantité de matières extractibles dans la pâte finale peut être beaucoup plus élevée. En raison de la plus forte teneur en acide résinique du bois infesté aux stades vert et rouge, un bon lavage de la pâte brune est particulièrement important dans les usines de pâte kraft. La forte teneur en acide résinique dans le bois entraîne une solubilité accrue d'acides gras et résiniques dans la liqueur résiduaire et une récupération du savon pratiquement nulle dans les usines de pâte kraft utilisant du bois au stage gris. L'utilisation de bois infesté dans les usines de pâtes et papiers fabriquant des pâtes thermomécaniques (TMP) n'a pas semblé provoquer de changements importants dans les quantités habituelles de matières extractibles et dans la composition chimique dans l'usine. L'utilisation d'un dispersant peut s'avérer nécessaire lors de la désintégration du bois infesté aux stades vert et rouge dans le but de prévenir le bourrage des rainures des plaques du raffineur. Les propriétés de friction du papier journal fait à partir de bois infesté sont restées dans la norme pour le papier journal. Le traitement des effluents des usines de pâte et papiers fabriquant des pâtes thermomécaniques a réussi avec succès à réduire les quantités de matières extractibles dans les effluents lors de l'utilisation de bois infesté pour les ramener à des valeurs tout près de zéro. Par contre, pour l'usine kraft utilisant du bois infesté au stade gris, la concentration d'acides résiniques dans l'effluent final était élevée.

Mots-clés : Dendroctone du pin ponderosa, pin tordu, matières extractibles du bois, matières extractibles, poix, acides gras, acides résiniques, stérols, stérols estérifiés, triglycérides, contrôle de la poix, transformation de la pâte et du papier, usines de pâte kraft, TMP, usines de papier, gestion des effluents, savon, récupération du savon, tallöl, friction, friction du papier, coefficient de friction

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1 Introduction

The work in this report was undertaken to address the concerns expressed by manufacturing personnel at western Canadian pulp and paper mills regarding the impact of using mountain pine beetle-affected wood on extractives-related issues in pulp manufacture. These concerns dealt with how the infestation will affect productivity, product quality, and manufacturing costs.

1.1 Extractives and their significance

Wood extractives comprise a complex suite of chemical compounds including volatile organic compounds such as the terpenes, resin and fatty acids, sterols, triglycerides, etc. (Ekman and Holmbom 2000), which serve numerous functions within trees. Primary amongst these functions is to act as a defense mechanism when an organism attacks a tree. The immediate response of a tree under attack by organisms, such as the mountain pine beetle, is to divert resources to generation of increased levels of extractives, especially toxic resin acids, in order to kill or "pitch out" the pest. In lodgepole pine under mountain pine beetle attack, extractives levels, in particular resin acids, can be much higher than in non-beetle-affected trees. The actual amounts of extractives and resin acids have been measured as a function of time since initial beetle attack, as part of the Natural Resources Canada, Canadian Forest Service Mountain Pine Beetle Initiative Project #8.42.

Wood extractives play many important roles in pulp and paper manufacture and they can affect product quality and effluent management. The production of tall oil soaps and the toxicity of the effluents may be increased when processing early (green) stage attack wood by the kraft process. Soap production is of economic importance to kraft pulping operations, as this material can be used to reduce the use of expensive fuel oil in lime kilns or recovery boilers or for the production of tall oil for fractionation into value-added chemicals. In mechanical pulp and papermaking operations, foam, pitch deposition and paper sheet slippage caused by changes in extractives may occur. As mills process older wood (where the time since death has increased), changes in extractives levels occur that may significantly affect mill economies in those mills using tall oil as an alternative energy source to fuel oil for lime kilns or those burning tall oil soap in recovery boilers to increase steam production.

As the mountain pine beetle epidemic has moved from the Cariboo region into Northern B.C., mills in different locations in the province have been using wood of varying degrees of time since infestation. This situation provides unique opportunity to map the process effects of wood of different qualities, to evaluate the means by which mills are managing extractives-related effects, and to coordinate operating guidelines and solutions to the changes in extractives content.

1.2 Tall oil soap recovery

Kraft pulping of softwoods converts the free resin and fatty acids and a large percentage of the triglycerides in wood into their sodium salts or "soaps". Associated with the salts are neutral or unsaponifiable compounds, such as sterols. The salts and unsaponifiable compounds separate from the spent cooking liquor as "black liquor soap". Wood species, dissolved solids content, and the residual effective alkalinity ($NaOH + \frac{1}{2} Na_2S$) in the black liquor can influence this separation (Foran 1992).

The recovered soap is either burnt in the recovery boiler or converted into a blend of fatty and resin acids and neutrals, known as "crude tall oil", through acidulation in a tall oil plant. About 12 kraft mills in Canada process recovered soap to produce 75,000 tonnes of crude tall oil (CTO) per year (Norman 1982). Although Canadian tall oil is generally of much lower quality than that from southern U.S. kraft mills (Norman 1982) and is often difficult to market, tall oil soap should be recovered to minimize its adverse affects on the unit operations in the kraft recovery system. In addition, tall oil has a higher heating value as high as 37.9 MJ/kg of dry solids (16,300 BTU/lb),

and many mills now burn tall oil in their lime kilns to displace a substantial portion of their purchased fossil fuel (Young 1989).

1.3 Effect of soap on evaporator scaling rates

The solubility of tall oil soap in pine black liquor from southern U.S. mills is highest in weak black liquor [more than 8 kg CTO (13.3 kg of soap)/oven dry tonne (odt) of liquor solids]. Soap solubility decreases as liquor is concentrated, passes through a minimum of about 3 kg CTO or 5 kg of soap/odt of dry black liquor solids at an intermediate concentration, then increases with increased solids concentration (Drew and Propst 1981). For this reason, soap is normally removed by skimming at an intermediate stage in evaporation. The soap that remains after skimming can precipitate on evaporator tube walls and soap has, in fact, been reported (Letonmyaki et al. 1964; Lamy, 1979) to be a significant component of evaporator and concentrator scale samples, particularly soluble sulfate-carbonate scales. In pilot plant evaporator studies (Uloth and Wong 1986), it was found that, although sodium scales form when the evaporator discharge solids approach or exceed the saturation concentration, soap greatly accelerates the rate of scaling. If all insoluble soap could be economically removed from a mill's liquor system, sodium scaling rates might be reduced by as much as 70%. In pilot plant studies at the Institute of Paper Chemistry (Frederick et al. 1977), it was similarly found that addition of tall oil soap, at a loading of approximately 17.4 kg soap (10.4 kg tall oil)/odt of dry liquor solids, increased the calcium carbonate scaling rate by 60% as compared with the original liquor.

1.4 Effect of soap on recovery boiler operation and capacity

Although it is well known that random fluctuations in the soap content of black liquor can cause undesirable variations in black liquor quality leading to unstable recovery boiler operation, the continuous burning of soap at low concentrations is often considered beneficial to recovery boiler operation. As the calorific value of soap is about twice that of heavy liquor, its presence in fired liquor increases steam-generating capability without adding to fuel costs. In addition, the presence of soap in fired liquor is thought to increase bed temperatures, thereby helping to control SO_2 emissions, reduce unburned carbon (dregs) and increase reduction efficiencies (Crouse and Stapley 1979). The sodium content of the soap, and the sulfur content of liquor normally entrained in skimmed soap, could also reduce chemical makeup costs when soap is burned.

The major disadvantage of burning soap is that it reduces the capacity to process black liquor in a recovery furnace that is limited either by plugging or steam production capacity. Using heat input calculations, measured gas temperatures and draft loss data, it was estimated that recovery boiler capacity in an 800 odt per day kraft mill could be increased by an equivalent of about 50 odt of pulp per day (6%) when soap was skimmed from the liquor system (Morgan 1979). In addition, it was found that the burning of soap, even at low concentrations, increased total reduced sulfur (TRS) emissions and boiler fouling rates at a given firing rate. Fouling was more widespread and more difficult to deal with effectively when soap was burned in these trials.

Using differential thermal analysis, it was shown that a connection may exist between liquor soap content and the occurrence of black-outs in kraft recovery furnaces (Kubes 1983). All the major Canadian softwood and hardwood species were cooked and their spent liquors were examined by chemical and thermal analysis. It was concluded that, at a constant ratio of organics to inorganics, wood species with high resin contents gave liquor solids that had high activation energies (i.e. hard to ignite). The addition of resins, extracted from jack pine, to the black liquor solids obtained from a kraft cook with black spruce increased the liquor activation energy substantially. Similarly, the addition of large amounts of soap to the black liquor obtained from cooking western hemlock in a pilot plant digester increased the liquor activation energy by a factor of approximately 2.7 (Milanova et al. 1985). Soap skimming from red pine and southern pine liquor samples was found to decrease the liquor activation energy by 30% to 40% (Milanova et al. 1985), leading the authors to conclude that the presence of soap adversely affects the burning of black liquor solids.

1.5 Factors affecting soap solubility and recovery

An excellent summary of the various laboratory and mill studies conducted to determine the factors affecting the recovery of soap was prepared by Drew and Propst (1981). The variables affecting soap recovery in the skim tank were reported to include the liquor solids content, liquor temperature, tall oil soap composition, liquor alkalinity and pH, liquor sulfidity and the ratio of hardwood to pine liquors. All of these studies were, however, conducted on southern pine liquors, and few of the studies considered more than one variable. The results of several of the reported studies were contradictory.

Studies on black liquor samples taken from several different Canadian mills (Uloth et al. 1987), including at least four kraft mills in British Columbia, were later undertaken at Paprican. Those studies showed that similar to the reported solubility behavior for soap in black liquors from southern U.S. mills, the solubility of tall oil soap decreased as black liquor was concentrated, passed through a minimum at an intermediate concentration and then increased slightly with increased solids concentrations. The most important factors affecting the soap solubility minimum were the soap composition and the residual effective alkali content of the black liquor. For soaps with a fatty acid/resin acid (FA/RA) ratio between 1.5 and 1.9, soap solubility was doubled if the residual effective alkali (REA) content of digester 17% to 20% solids extraction liquor was reduced from 10 g/L to 6 g/L as Na_2O (i.e. from about 5.3% to 3.2% REA on dry black liquor solids). As the FA/RA ratio in the soap increased, the minimum soap solubility and the REA concentration needed to minimize soap solubility decreased. The effect of hardwood liquor, which contains mostly fatty acids soaps but generally has lower REA than softwood black liquor, was found to depend on the fatty acid/resin acid ratio in the resulting soap and the REA concentration in the mixed black liquors. The results of these studies were useful in explaining many of the phenomena observed in mills that alternately pulp hardwood and softwood species (Lenz 1977; Foran 1992).

1.6 Effect of pulping mountain pine beetle-affected wood on soap recovery

Accelerated harvesting of beetle killed wood in British Columbia has changed the wood species mix coming into kraft mills and the amount and behavior of the extractives. Although the amount of pine in the wood furnish has universally increased, which would be expected to increase the extractives levels in liquors and tall oil soap recovery, different mills in B.C. have observed widely varying effects on tall oil soap recovery. Some mills report being flooded with tall oil soap, whereas others have had to shut down their tall oil plants because they no longer skim enough soap to make operation of the tall oil plant economical. A drop in soap recovery and tall oil production can have serious negative economic impacts on a mill, particularly mills that are recovery limited or those that burn the product tall oil in their lime kilns. Studies were clearly required to determine why different B.C. mills are seeing very different impacts of pulping beetle-affected wood on tall oil soap recovery. Studies were also needed to help many of the affected mills better understand the effects of increases in soap content in the fired liquor and how to deal with higher extractives levels in the fired black liquor.

2 Material and methods

2.1 Mills actively involved in the project

Shown in Table 1 are the mills that participated in this project.

Table 1. Participating mills

Kraft Pulp Mills	Mechanical Pulp Mills	Paper Mills
Canfor Pulp Ltd. Partnership, Northwood Pulp Mill, Prince George	Catalyst Paper, Powell River	Catalyst Paper, Powell River
Cariboo Pulp & Paper Co., Quesnel	Howe Sound Pulp & Paper Ltd., Port Mellon	Howe Sound Pulp & Paper, Port Mellon
Pope & Talbot Ltd., Mackenzie	Abitibi-Consolidated Inc., Mackenzie	Abitibi-Consolidated Inc., Mackenzie
Canfor Pulp Ltd. Partnership, Prince George Pulp & Paper Mill, Prince George		Canfor Pulp Ltd. Partnership, (Prince George Pulp & Paper), Prince George
Weyerhaeuser Co. Ltd., Grande Prairie		

In the original proposal for this project, the Canfor BCTMP mill at Taylor, B.C., was included. The plan to use this mill was abandoned when we realized that it was a mill that used spruce as its predominant species. In addition, the original proposal included Quesnel River Pulp; this mill site was eliminated and the Howe Sound Pulp & Paper mill was substituted, so that we had several newsprint mills in the study for comparison. The Catalyst, Powell River, TMP plant was also added to the list of mechanical pulp mills since the original proposal was submitted.

As some of the information collected is potentially sensitive for the mills involved, they have been identified in this report as Mills A, B, C, etc. Personnel of participating mills can obtain the identity of their mill by contacting the authors.

2.2 Extractives analysis protocols

We measured the extractives profile across each mill. This involved analyzing the extractives obtained from samples of: chips, pulps at key points along the process, black liquor samples, and final product at each mill. To minimize the effects of minor variations in wood processed in the mill from one minute to the next, we arranged for composite sampling, consisting of six samples taken one hour apart. For the sampling along the fibre line, we initially attempted to follow the pulp as it proceeded through the mill. Unfortunately, this proved to be too cumbersome, and after the first mill we abandoned it in favor of sampling about six times during an 8-hour shift. In all cases, sampling was conducted only when the mill was running in steady state, so that attempting to follow the same pulp as it proceeded through the mill was felt to be less important.

Samples were shipped to Paprican. For acetone extraction, they were freeze dried and then extracted using a 2050 Soxtec Extraction System (Foss, Eden Prairie, MN). They were then methylated and analyzed by gas chromatography for major classes of components. For liquid samples, the extractions were done in a separatory funnel, using the Saltsman technique for black liquor samples (Saltsman and Kuiken 1959) and methyl-t-butyl ether as a solvent for the effluent samples. For the latter, filtration was done first through an acetone-washed glass-fibre (Whatman G/F) filter. The residue and filtrate were then extracted and analyzed. The residue was first freeze dried and then extracted with acetone.

For each effluent filtrate sample, a 50-mL portion of the filtered liquid was adjusted to a pH of 9. The sample was transferred to a 250-mL separatory funnel and extracted twice with 50 mL of methyl tertiary butyl ether (MTBE, high-performance liquid chromatography (HPLC) grade). The organic layers were collected, dried with sodium sulfate, evaporated using a BUCHI R110 rotary evaporator to a few milliliters, then transferred to a 20-mL pre-cleaned vial. The vial was placed

in a heating block (Reacti-Therm, Pierce, Rockford, IL) set at a low temperature and was evaporated to dryness under a stream of nitrogen. The dried residue was analyzed by gas chromatography for the classes of compounds found in wood extractives.

The sample preparation and extraction of pulp samples was done as follows. Portions corresponding to 20 g to 25 g oven-dried (O.D.) pulp were freeze dried prior to extraction. Samples with low consistencies, such as headbox pulps and white waters, were freeze dried in three to four polyethylene bags (2.5"x 8"), and the dried solids were combined for extraction. Acetone extraction was performed on 4 g to 6 g of dried samples using a 2050 Soxtec Extraction System (Foss). This automated extraction system is based on a Soxhlet extraction, but here the sample is boiled in the solvent for one hour, raised over the solvent and rinsed with freshly condensed solvent for another hour. Finally, evaporation is performed with the system to a few millilitres. The remaining solvent was transferred to a pre-weighed, 20-mL vial. The final drying was done by placing vials in a heating block (Reacti-Therm, Pierce) set at a low temperature under a gentle stream of nitrogen, followed by freeze drying overnight to remove residual solvent. The vials were then weighed, and total extractives could be calculated.

The preparation of a calibration mixture and internal standard solution prior to gas chromatographic analysis was done as described below. The following organic compounds, listed under their classes of extractives component, were mixed as a stock solution at approximately 1 mg/mL for each compound in chloroform. A separate stock solution of cholesterol at about 1 mg/mL in chloroform was prepared and used as an internal standard.

Fatty acids, alcohols and monoglycerides

- Palmitic acid
- Octadecanol
- Oleic acid
- Linoleic acid
- Stearic acid
- Stearolic acid
- Heneicosanoic acid
- Docosanol
- Monopalmitin
- Tricosanoic acid
- Tetracosanol
- Monostearin
- Tetracosanoic acid

Resin acids

- Pimaric acid
- Dehydroabietic acid
- Abietic acid
- Neoabietic acid

Sterols

- Campesterol
- Stigmasterol
- Beta-sitosterol
- Stigmastanol

Fatty acid steryl esters (Wax esters)

- Palmitic acid steryl ester

- Tricaprin
- Betulin
- Stearic acid steryl ester
- Behenic acid steryl ester

Diglycerides

- 1,3 Dipalmitin
- 1,3-Distearin

Cholesteryl Ester

- Cholesterol stearate

Triglycerides

- Trimyristin
- Tripalmitin
- Tristearin
- Trinonadecanoin

The compounds listed above were 95% to 99% pure and used with no further purification. Chloroform used for the solutions was HPLC grade.

Analysis of fatty and resin acids by gas chromatography requires adding a methyl group to the acid moiety in order to enhance the chromatographic sensitivity and peak shape. Diazomethane derivatization of extractives prior to gas chromatographic analysis was conducted in the following way. From the standards solutions, a calibration standard was prepared with 100 µL of each standards solution in a 1.5-mL vial. The vial was placed in a heating block (Reacti-Therm, Pierce) set at a low temperature, and the solvent was evaporated under a gentle stream of nitrogen. A blank consisting of only the internal standard was prepared along with the samples. The solvent was evaporated in the same way as described previously. Based on extractives weights of the samples, about 8 mg to 10 mg of extract and 100 µL of internal standard were transferred into a 1.5-mL vial. If less extract was available, the entire extract was used. The solvent was evaporated as described above. One millilitre of methanol/MTBE 9:1 was added to the dried extracts and standards. The derivatization was done by bubbling diazomethane gas for 5 minutes into the sample from a diazomethane generator (Sitholé et al. 1992). The solvent was evaporated in a heating block, as described above. Then 0.5 mL chloroform was added to the dried residue, the vial was capped, and the contents were well mixed prior to analysis by gas chromatography.

Gas chromatography and data analysis were done as follows. A Hewlett-Packard 5890 Series II gas chromatograph equipped with a flame ionization detector, an electronic pressure control capillary inlet system and a HP7673 automatic injector was employed. The chromatograph was interfaced with a Dell Pentium II for data collection and processing, with HP Chemstation Ver.10.01 software packages (Agilent, Santa Clara, CA) on a Windows XP Professional (Microsoft Corp., Seattle) operating system. A DB-5HT column, 30 m x 0.25 mm internal diameter x 0.1 µm film thickness was used. Ultra-high purity helium was used as the carrier gas.

The temperature program for a run was as follows: start at 100° C and hold for 5 minutes, heat to 200° C at 10° C/min and hold for 3 min, then heat to 245° C at 2° C/min, and finally heat to 360° C at 10° C/min and hold for 10 min. Total run time was 62 min. The injection port was set at 360° C. The pressure program was set at 140 kPa (20.4 psi) at 100° C to obtain a constant flow of 1.6 mL/min throughout the analysis, and the split ratio was 40:1 for sample volumes of 1 µL injected into a deactivated glass liner used in the injection port. The flame ionization detector temperature was set at 370° C

For data analysis, a calibration table was built from calibration standard runs and sample runs were processed from it. The report generated was saved as a text file and used on Excel spreadsheet software (Microsoft Corp.) to compute the concentration of each class of components. Each component class was determined using retention time windows (Sitholé et al. 1992) as presented in Figure 1.

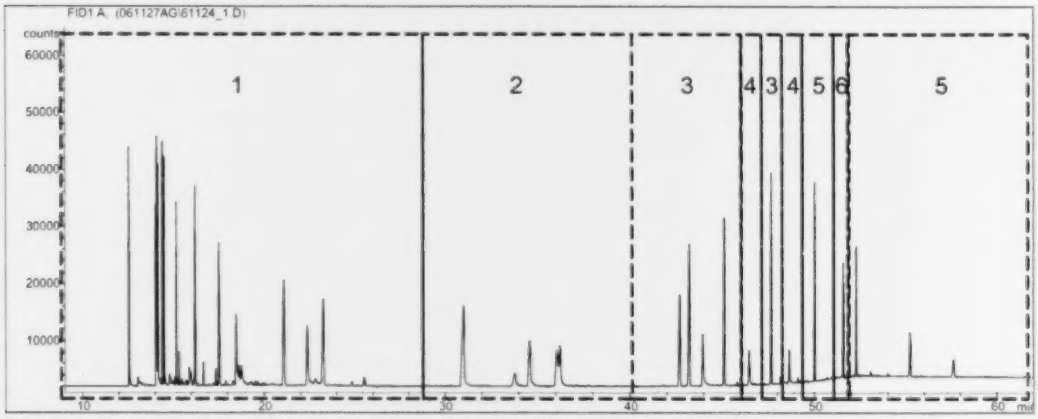

Figure 1. Example of retention time windows from a calibrated run, and model compounds used to calculate the relative response factor (RRF) applied on unknown compounds from each class.

Table 2. Retention Time Windows

Window Number	Class of compound	Model compound
1	Fatty acids, resin acids, fatty alcohols and monoglycerides	Stearic acid
2	Sterols	Stigmasterol
3	Wax esters	Stearic Acid Steryl Ester
4	Diglycerides	1,3-Dipalmitin, 1,4-Distearin
5	Triglycerides	Trimyristin, Tripalmitin
6	Cholesteryl Esters	Cholesterol Stearate

The analysis of deposit samples involved (as appropriate): freeze-drying, ashing, carbonate analysis, sequential extraction with acetone and chloroform, solid phase extraction of the acetone extract (Sitholé and Filion 2005), FTIR analyses of the sample and its extracts, gas chromatography analysis of the extracts as described above, and pyrolysis gas chromatography/mass spectrometry (Sitholé et al. 1994).

2.3 Extractives profiling

The profiling of extractives at participating pulp and paper mills involved a visit of several days to each mill. During each visit, samples required for the extractives profiles were discussed, as were sampling protocols, as described above.

In addition, information important to extractives-related problems was gathered. The mill was then inspected for present deposition patterns and operating details important for pitch control. If

available, deposit samples were collected.

At the end of each visit, there was an exit conference with mill staff to highlight the vulnerabilities of the mill to pitch problems as the process was operated at the time of the visit. In all cases, recommendations were made for improvement. This was necessary, as there are many factors that contribute to whether or not a mill has pitch problems. High extractives is but one of them. Nevertheless, if a mill is operating on the edge of having a pitch problem, higher extractives will likely precipitate problems. These problems usually take the form of deposits in the mill, which can cause problems in productivity. Often, the worst outcome is pitch-dirt in the final product, which can cost mills hundreds of thousands of dollars per week due to the necessity of selling the contaminated pulp or paper at a discount.

An important parameter that was needed from each mill visit was a good estimate of the degree of mountain pine beetle infestation. In addition to the estimate given by mill staff, a sample of chips was taken for subsequent measurement of: extractives content, percent blue stain, and percent pine. This sampling was to enable estimation of degree of infestation of the chip source being consumed by the mill at time of sampling.

2.4 Analysis and reporting

For each operation, an "extractives profile" was generated and related to incoming chip quality (green-, red-, and/or gray-stage). This consisted of a bar chart showing the amounts of extractives in the pulp at various stages of the process and ending with the final product. A similar profile was constructed for the resin acid content (Appendix I).

Extractives concentration and resin acids content were correlated with coefficient of friction (COF) for paper mills to more precisely determine whether there was an effect of mountain pine beetle on the friction properties of paper. For this work, the friction properties were determined using (Technical Association of the Pulp and Paper Industry) TAPPI Test Method T549 (Anonymous, 2006).

2.5 Tall oil soap recovery

2.5.1 Tall oil soap solubility studies

Tall oil soap solubility as a function of black liquor solids content was investigated using black liquor and tall oil soap samples from five kraft mills. One day composite weak (17% to 20% solids) and strong (48% to 55% solids) black liquor samples, comprised of at least three grab samples taken over the course of the day, were obtained from each mill. Each of the B.C. mills also supplied a sample of tall oil soap skimmed on the day that the black liquor samples were collected. By mixing various proportions of unskimmed weak black liquor and skimmed strong black liquor, liquors with solids levels between 18% and 55% were obtained. Water was also mixed with the weak black liquor to prepare one low solids sample (15% to 16%) in each test series. These samples were mixed and transferred into 250 mL graduated cylinders, which were then covered and placed in an oven at 90° C. The samples were allowed to sit undisturbed for 6 to 7 hours. As earlier studies (Lenz 1977; Uloth et al. 1987) reported complete phase separation after 10 to 20 minutes under laboratory conditions, the 6 to 7 hours of separation time used here should have been more than adequate to ensure equilibrium conditions and complete tall oil soap separation. The insoluble soap was skimmed from the surface of each sample using rolled paper towels and the still-hot "skimmed" liquor was then sampled using a pipette inserted well below the liquor surface. Care was taken at all times to wipe any soap from the external surface of the pipette prior to depositing the sample into a second sample bottle for ultimate analysis. The crude tall oil (CTO) content of the skimmed liquor was determined using the Saltsman and Kuiken procedure (1959). The crude tall oil (CTO) content of the skimmed liquor was converted to soap content by assuming a 60% yield of CTO from soap (Uloth et al. 1987). Attempts were then made to correlate the effect of operating variables, such as black liquor residual effective alkali content,

initial soap content and soap quality (fatty and resin acid ratio) on these soap solubility curves and the soap solubility minimum in particular.

Composite samples of the weak and strong black liquor were also taken at each mill and diluted to less than 10% solids to ensure complete soap solubility. The solids and tall oil content of each of these samples were also determined. Because soap content of several weak black liquor samples was low, a second series of soap solubility tests was run for three of the B.C. mills. In the second series of tests, a sample of soap was added to each of the blended liquor samples to ensure that the soap content exceeded the solubility limit. The blended liquors and added soap in a sample bottle, at close to 90° C, were shaken well before being transferred to a 250-mL graduated cylinder and placed in the constant-temperature oven. These samples were skimmed after 6 to 7 hours separation time and analyzed as detailed in the preceding paragraph.

2.5.2 Seasonal variations in soap composition

Samples of the soap skimmed in each of the four B.C. kraft mills were also taken each month and forwarded to our laboratory. The Alberta mill did not actively recover soap and was thus unable to provide us with such monthly samples. Duplicate portions of these soap samples were acidulated and extracted to estimate a potential tall oil yield using Pulp Chemicals Association Test Method (PCTM) 7 (1996). The extracted tall oil was then analyzed. One portion was used to determine the tall oil acid number (PCTM 1 1996), a measure of the free resin and fatty acids in the tall oil that is widely used to assess quality. The second extract was analyzed for resin acids using a wet chemical method (PCTM 17 1996). The results of the acid number and resin acid determinations were then used to estimate the fatty acid content of each soap sample (PCTM 20 2002) and the fatty acid/resin acid ratio of the soap recovered at each mill.

2.5.3 Effect of soap on black liquor properties

The viscosities of black liquor samples with various amounts of soap added were measured using a Haake rotating-cylinder pressurized viscometer (Rotovisco RV30). The Haake pressurized viscometer has a maximum shear rate of 500 s^{-1} (comparable to the shear rates seen in falling film evaporators) and can be used to measure liquor viscosities up to about 10,000 cP. It is equipped with an oil bath and has a maximum operating temperature of 300° C. Because this viscometer is pressurized, with a maximum operating pressure of 100 bar, viscosity can be measured at or above typical black liquor firing temperatures. The viscometer was calibrated with oils of known viscosities. Black liquor samples, with soap added in various proportions, were heated in full, closed bottles to prevent oxidation and thoroughly mixed by shaking before being transferred to the viscometer.

2.5.4 Analytical

The Saltsman and Kuiken method (1959) used to determine the soap content of black liquor consists of: i) acidulation of a black liquor sample, ii) extraction of CTO from the acidulated mixture, and iii) weighing the dried extracted tall oil. The standard deviation of the test was found to be 0.2 kg/odt of dry liquor solids for a liquor sample with a tall oil content of 5.0 kg/odt of dry liquor solids. Recovery efficiency for tall oil added to black liquor ranged from 91% to 98% (Uloth et al. 1987). The residual effective alkali content of digester extraction liquors was determined using a modification of the standard PAPTAC (Pulp and Paper Technical Association of Canada) test procedure (Method J.15P) detailed in an earlier paper (Milanova and Dorris 1994).

The higher heating value (HHV) of black liquor samples, with and without soap addition, was determined according to TAPPI Test Method T684 om-02, using bomb calorimetry. In this method, the latent heat of water and the heat of oxidation of sulfur are included in the measured value. To obtain the actual heat available in black liquor solids in the recovery boiler (i.e., the net heating value, NHV), a correction for contributions from hydrogen and sulfur needs to be made. Black liquor solids were determined according to TAPPI test method T-650-om-99, where sand is

used to provide an extended surface for drying and to prevent the formation of crusts that trap moisture inside the drying liquor. The soap content of the liquors was determined by the difference between an acidic extraction and an alkaline extraction (Douek and Allen 1980). For swelling index, a modified version of the procedure outlined by Milanova et al. (1985) was used.

3 Results and discussion

3.1 Acetone extractives at key points in the process

3.1.1 Kraft mills

Shown in Figure 2 are the acetone extractives derived at various stages in the process for the five kraft mills. Mills B, C and D do not have oxygen delignification, and Mill C was producing semi-bleached pulp at the time of sampling. Based on previous experience (Allen and Lapointe 1987), the amounts of acetone extractives in all of the mills are in the normal range. Even if all the mills were using the same chip supply, there would be some mill-to-mill variation in amounts of extractives at various points, due to mill-specific conditions such as the temperature of early brownstock washing, the efficiency of brownstock washing in particular (but also of the bleach plant washers), washer filtrate recycling practices, degree of system closure in the mill, defoamer use, etc. As Figure 2 demonstrates, as the mills go from using almost non-beetle-affected fibre (Mill A) to mostly gray-stage fibre (Mill E), there are no dramatic trends. Most notably, one might have expected Mills B, C and D to have higher extractives than Mill A, which used non-affected wood, and Mill E, which used gray-stage wood. This is based on the hypothesis that during attack, when a tree is attempting to pitch out beetles, production of canal resin by parenchyma cells is at peak, and one might therefore expect higher extractives content in the wood. This is not observed in Figure 2, probably because the excess resin is removed with the bark and/or unbleached washing.

A softwood kraft pulp mill should be able to produce pulp with less than 0.05% acetone extracts. Only one mill was unable to achieve this, and it was using mostly gray-stage wood. In Mill E, the Eop extractives are similar to those at Mills A to D. (See Section 3.2.1 for examination of the higher extractives contents in the final pulp at Mill E.)

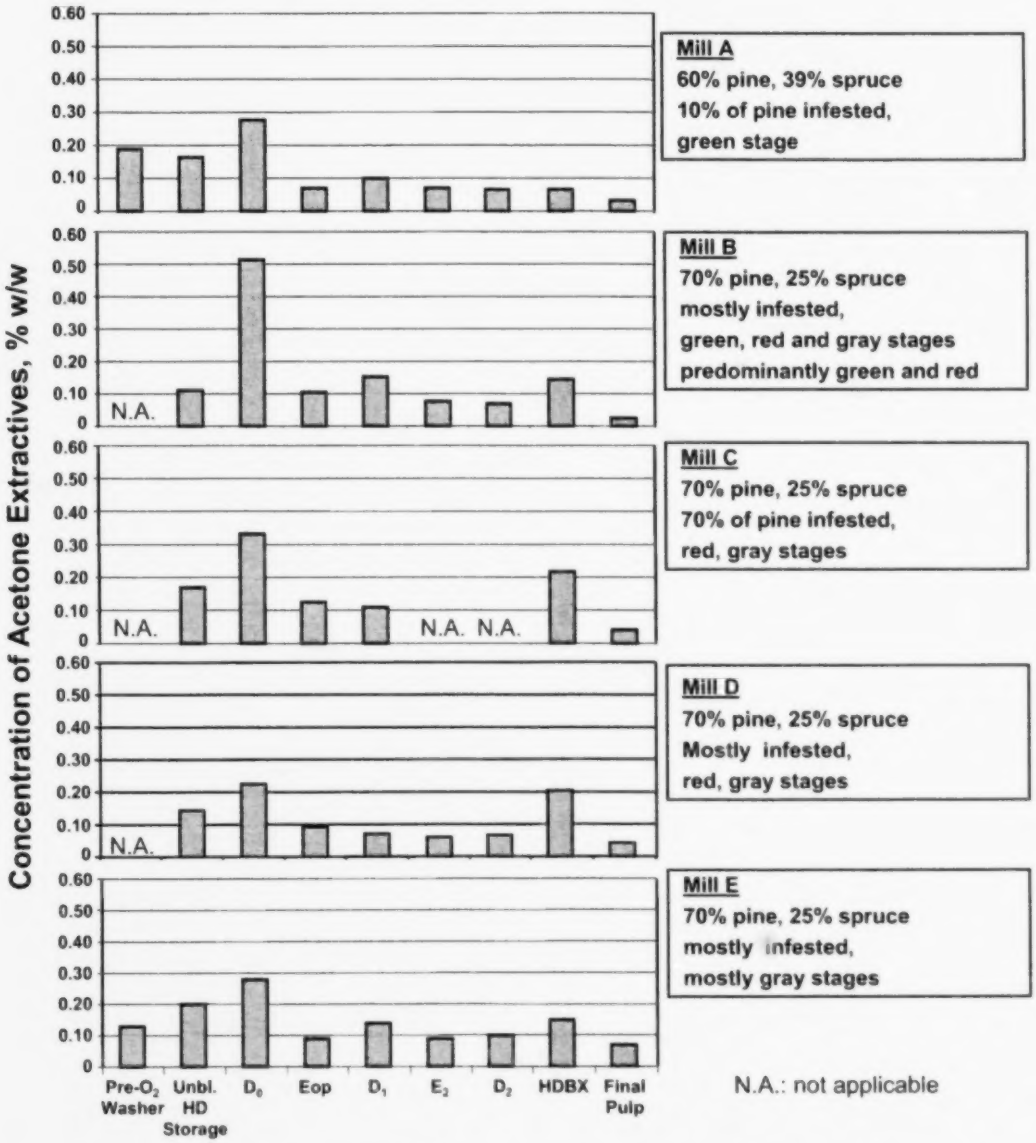

Figure 2. For the kraft mills, concentration of acetone extractives (% by weight on dry pulp) versus sampling point along the process stream. Mills have been arranged so that the time of infestation of wood used increases in proceeding from top to bottom.
Note: Indicated for each mill, to the right of the bar graph, is the mill's assessment of the state of infestation of its pine wood and the percent pine in the furnish. The mills have been placed in this figure so that they go from almost pre-infestation (Mill A) to mostly gray stage (Mill E) as we read down the figure.
Definitions: Pre-O_2 Washer, washer before oxygen delignification; Unbl. HD Storage, unbleached high density storage tank; D_0, D_1, D_2 , successive chlorine dioxide stages of bleaching; Eop, caustic soda stage of bleaching with added oxygen and peroxide; E_2, second caustic stage of bleaching; HDBX, pulp machine headbox.

According to data presented in Figure 2, at most mills, the D_0 and pulp machine headbox samples have higher extractives than samples from points on either side of these stages in the mill. This is normal. The D_0 acetone extractives of pulp are usually high, because the pH at this stage is less

than 3, which results in the extractives dispersed in the process water being coagulated onto the fibres (Allen and Lapointe 1987). These precipitated extractives are later redispersed in the Eop stage and further washed from the pulp. The extractives in the headbox samples are high due to the recirculation of pulp machine white water. This results in a build-up of the dispersed extractives and fines rich in extractives (Allen and Maine 1978; Ricard and Dorris 2006).

3.1.2 TMP mills

Figure 3 presents the concentrations of acetone extractives at three stages along the process line in the participating TMP plants. Two of the TMP mills also produced peroxide-bleached TMP, whereas Mill F did not.

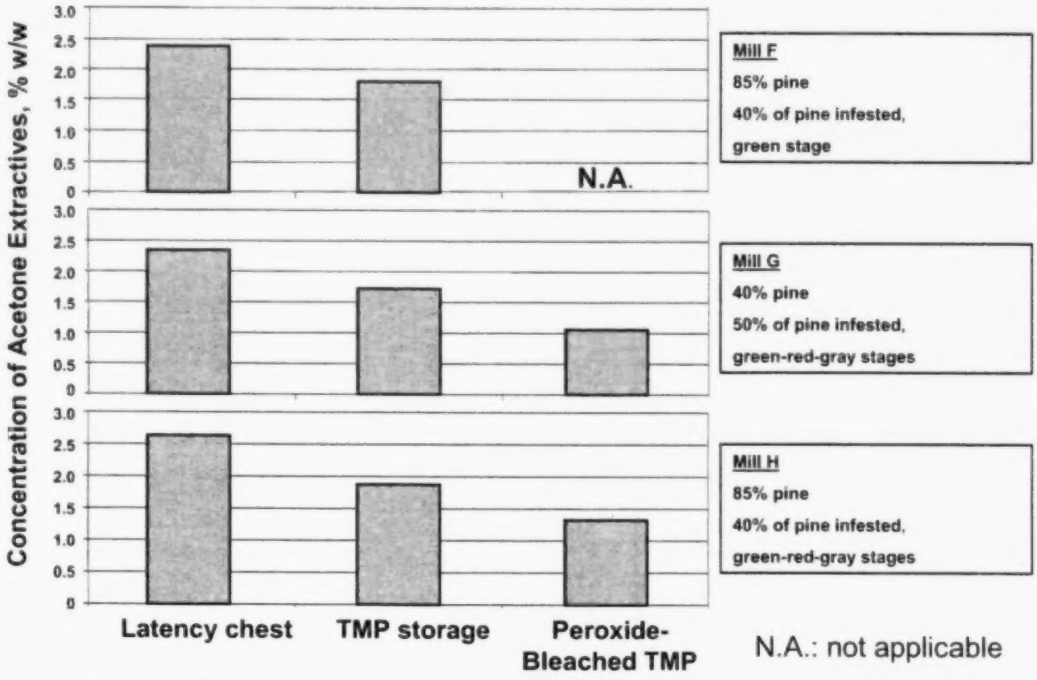

Figure 3. For the TMP mills, concentration of acetone extractives versus sampling point along the process stream. Mills have been arranged so that the time of infestation of wood used increases in proceeding from top to bottom.

The acetone extractives are about the same at the latency chests in all three mills. As might be expected, the extractives decreased as the pulp proceeds through the plant (left to right). The amounts of resin observed in these mills are normal and there is no trend from top (green-stage fibre) to bottom (green-, red-, gray-stage fibre).

3.1.3 Paper mills

The acetone extractives at key points in the paper mills are provided in Figure 4. For Mill H, we have included results for two paper machines. As might be expected from the extractives in their TMP plants indicated in Figure 3, the extractives in the paper mills are normal and within the usual range observed for paper mills using mechanical pulps. It is worth noting that Mill H employs precipitated calcium carbonate (PCC) fillers in its papermaking furnishes: these absorb extractives, which results in less dissolved and dispersed extractives concentrating in the recirculated white water. Hence the paper machine headbox and white water samples are lower in extractives content, but the final paper is about the same as for Mills F and G.

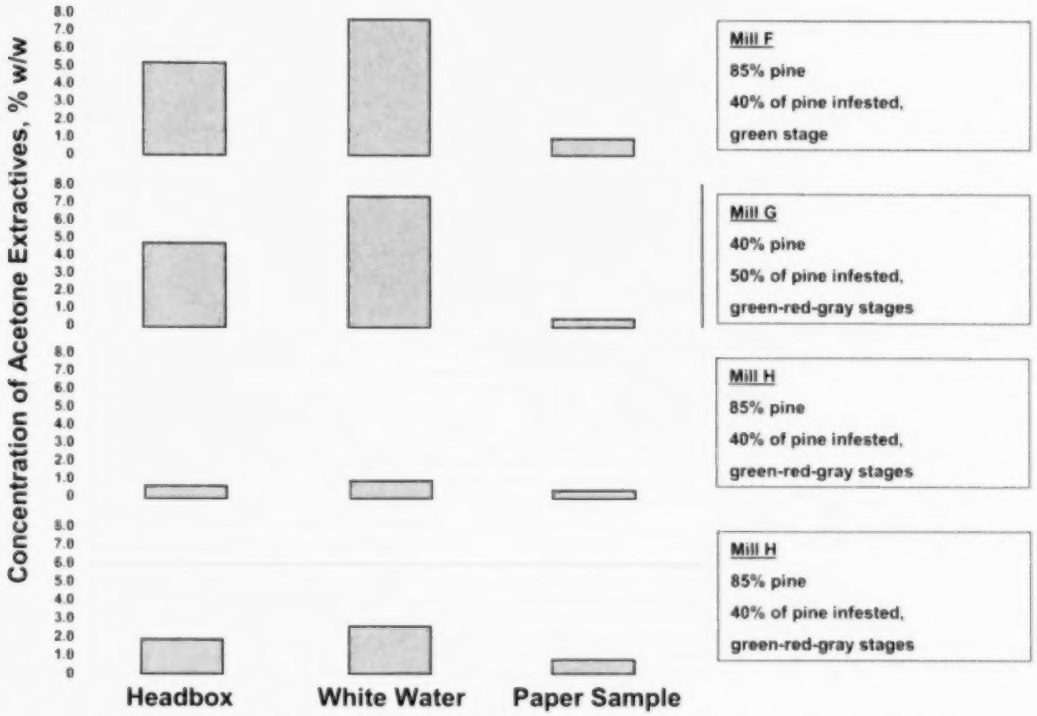

Figure 4. For the paper mills, concentration of acetone extractives versus sampling point along the process stream. Mills have been arranged so that the time of infestation of wood used increases in proceeding from top to bottom. Mill H has several paper machines, two of which are represented here.

There is no trend apparent in going from Mill F (green-stage fibre) to Mill G (green-, red-, gray–stage fibre).

3.2 Composition of acetone extractives in mills

3.2.1 Kraft mills

Figure 5 presents data on the composition of the acetone extractives at various posts along the process stream in the five kraft mills. Usually in kraft mills, the fatty acids predominate in such analyses and are followed by the resin acids and sterols. This trend is followed throughout Figure 5. Furthermore, in softwood kraft mills, diglycerides and triglycerides are usually absent, because they are saponified in the digester. The sterol esters are also largely saponified and are present only in trace amounts.

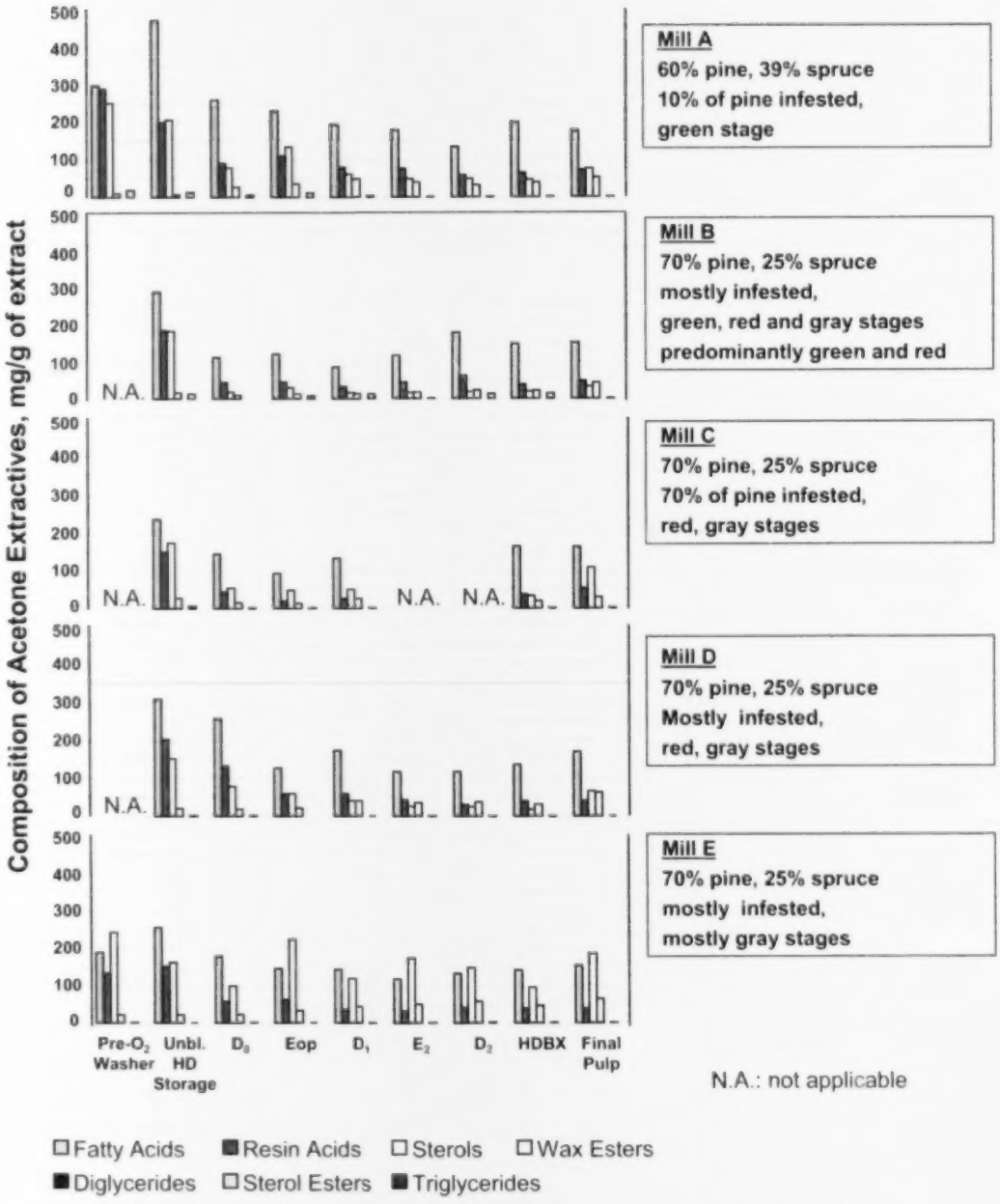

Figure 5. For the kraft mills, composition of the acetone extractives versus sampling point along the process stream. Time of infestation of wood used increases in proceeding from top to bottom.

In Mill E (mostly gray–stage beetle-affected wood), the amounts of sterols and wax esters are significantly higher. These classes of compounds are often referred to as unsaponifiables and are know to be less easily washed from the pulp due to their very hydrophobic nature. The presence

of resin and fatty acids in micellar form (aggregates of soap ions oriented with their hydrocarbon tails together in the interiors usually of spherical particles) in black liquor and pulp during unbleached washing offer a mechanism for the solubilization of unsaponifiables and their removal in brownstock washing (Allen and Lapointe 2003). Because fatty and resin acid soaps are more soluble in gray-stage black liquor (see Section 3.5 Tall oil soap recovery), this mechanism of deresination is all or partially lost. This is very likely the reason for the higher extractives in the final pulp of Mill E (Figure 2).

The data presented in Figure 5 indicates that beginning at the D_0 stage and downstream in the process, the yields of extractives from the gas chromatographic column are lower. This is attributable to partial chlorination of the double bonds in the extractives molecules, which renders them more difficult to identify in gas chromatography. In addition, some oxidation and polymerization may be occurring, which would also contribute to a lower yield in the chromatographic column. Unfortunately, in its present stage of development, analytical chemical technology does not enable good quantitation of chlorinated, oxidized and/or polymerized extractives.

3.2.2 Thermomechanical pulps

Figure 6 presents the composition of the acetone extractives of the TMP pulp samples taken at three points along the process stream. All of the analyses represented are normal breakdowns for the acetone extractives in mechanical pulps. Furthermore, within the experimental error of measurement and the variability in the mills due to changes in wood being used from hour to hour, the composition is about the same in all three mills, despite Mill F using green-stage wood and Mills G and H using a mix of green-, red-, and gray-stage wood.

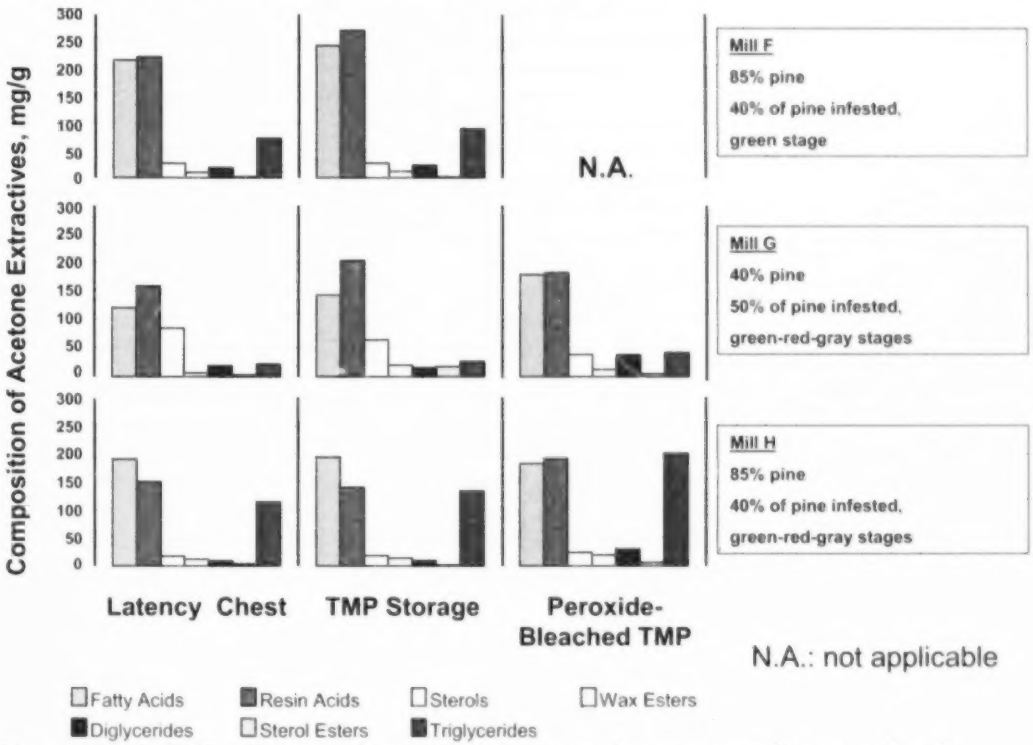

Figure 6. For the TMP mills, composition of the acetone extractives versus sampling point along the process stream. Time of infestation of wood used increases when proceeding from top to bottom.

An observation from the data in Figure 6 concerns the triglyceride content of the extractives: these are highest in Mill H and lowest in Mill G. High glycerides indicate freshly cut wood, whereas low glycerides indicate wood that has been stored or "seasoned" since cutting. As both Mills G and H were using purchased chips, mill personnel were not aware of any reasons why the chips furnished to one mill should be better seasoned than to the other, except that normal handling of the wood does involve storage (storage of roundwood in forest, trucking to sawmill, storage at sawmill, storage of slabs prior to chipping, storage of chips prior to transportation, transportation to the mill). Both Mills G and H did not retain large inventories of chips and often "hot-loaded" chips directly from the barge in an effort to achieve higher pulp brightness.

3.2.3 Paper mills

Following the trend observed in the preceding figure for TMP mills, it is not surprising that the analyses of the corresponding paper mill samples (Figure 7) are normal and do not show a trend from green stage (Mill F) to the more advanced stages of beetle effects on wood used by the other mills.

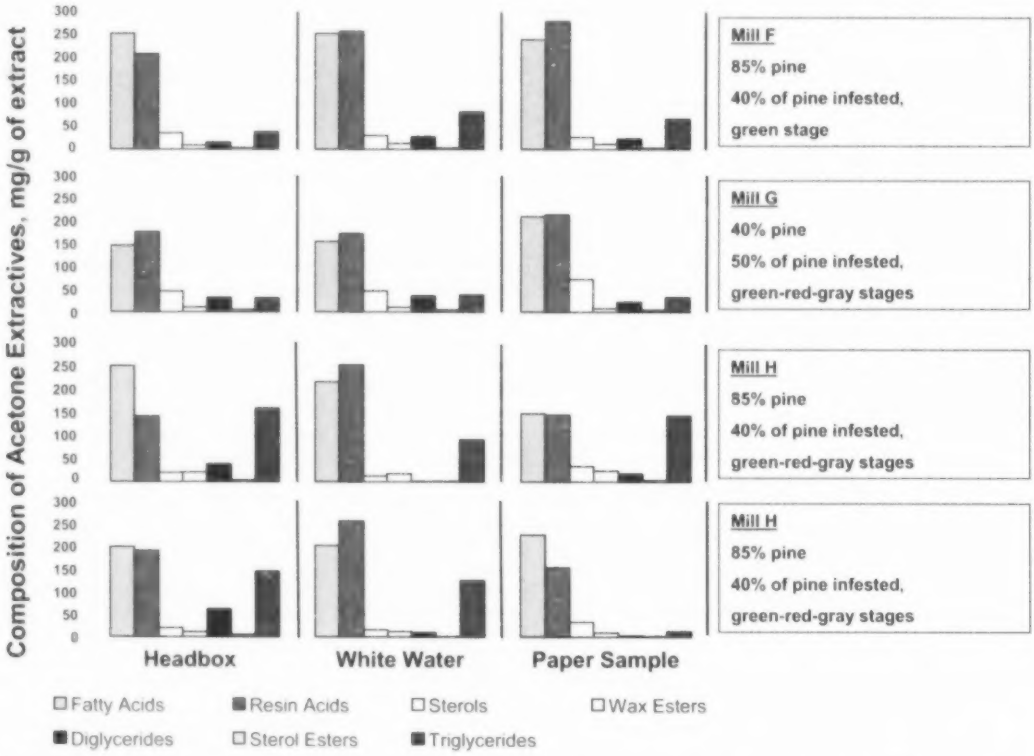

Figure 7. For the paper mills, composition of acetone extractives versus sampling point along the process stream. Time of infestation increases in proceeding from top to bottom. Mill H has several paper machines, two of which have been represented.

The higher glycerides content in Mills F and H are again evident. The reason for the low triglycerides content in the second paper sample from Mill H is unclear. This low value is not reflected in the headbox and white water samples, so the result can probably be considered an outlier.

3.2.4 Analyses of chips for extractives, blue-stain fungi and percent pine

Shown in Figure 8 are the data on the chip samples collected at the mills and sent to Paprican for analysis. The samples from Mill A did not arrive, and we received only one sample for Mills C and D, which were very similar in wood supply, so they have been grouped together in Figure 8. The percent pine (brown bars) is in reasonable agreement with the mill estimates given in the legends of Figures 2 and 3. Percent blue-stained chips tends to mirror percent pine. Mill E (gray-stage wood) has a proportionately higher percent blue-stained chips.

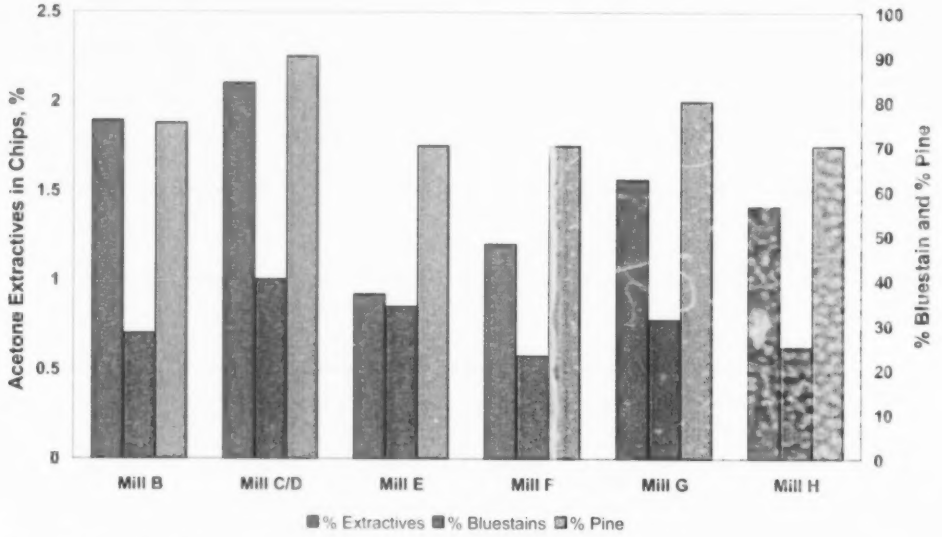

Figure 8. For the chip samples, acetone extractives, % blue stain and % pine.

Figure 9 gives the chemical composition of the extractives in the chips. It is evident that triglycerides are missing or are low in most of the chip samples. This indicates old chips and is inconsistent with the data in Figure 6, where it would appear that amounts of triglycerides are appreciable in the TMP pulp samples. (They are zero in all the kraft pulp samples due to normal saponification in the kraft digester). This has led us to conclude that the extractives in the chip samples aged during the time required for transport to the lab (transportation often took at least one and sometimes several weeks). Triglycerides hydrolyze with chip storage and this occurs quickly initially and then slows with time (Nugent et al. 1977; Ekman 2000). Usually it takes about six weeks for the triglycerides content of chips to drop to zero. Causes for their disappearance include continued metabolic activity within the wood, enzymatic hydrolysis, and breakdown by fungal activity. Because none of these processes occurs in the TMP pulps during transportation and storage, their extractives composition better reflects the composition of the chips at the time of pulping.

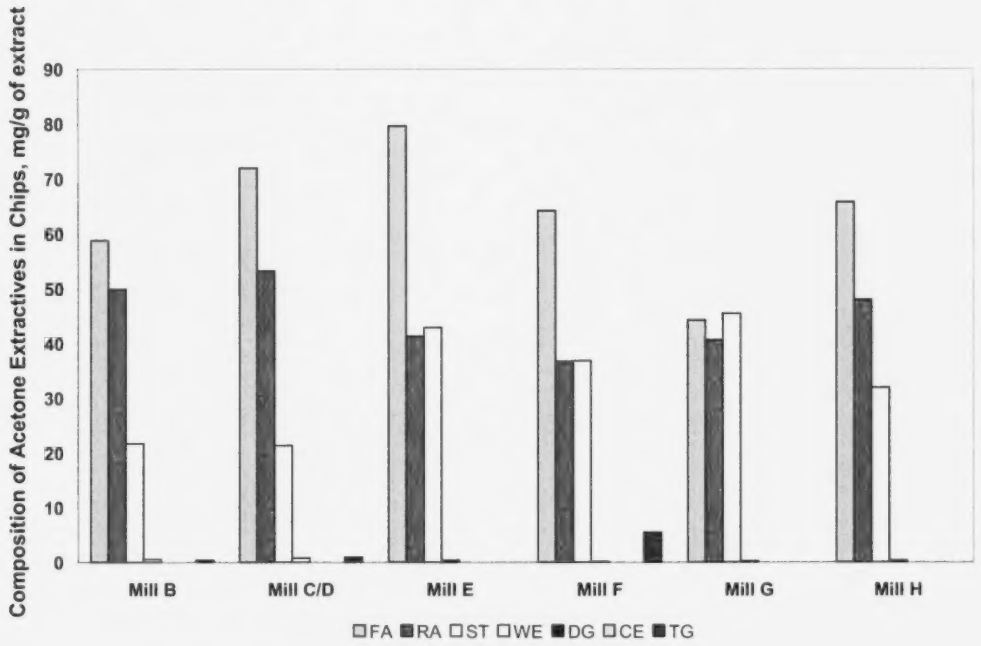

Figure 9. Composition of acetone extractives in chips.

We originally intended to include chip extractives and their composition among the data presented in Figures 2 to 7; however, the hydrolysis of glycerides during transport led us to conclude that the chip analyses were no longer truly representative of what the mill was using at the time of collection.

We also intended to use the chip data in Figure 8 to rank the mills according to state of infestation, as shown by percent blue-stained wood. On further reflection, we concluded that the mill data and estimates are more reliable than the "snapshot in time" we could obtain from one composite sampling over an eight-hour period. Therefore, the rankings in the figure legends (e.g., Figures 2 to 4) are based on mill data given to us during the site visits.

3.3 Composition of acetone extractives in sewered waters

3.3.1 Kraft mills

The compositions of acetone extractives in the sewered water to the primary clarifier, secondary treatment and final outfalls are presented in Figure 10. In Figures 10 and 11, the contributions are divided into those from the solid phase (lower section of each bar) and the water phase (upper section of each bar).

Considering the sewer water to the primary clarifier in Figure 10, it appears that the extractives were highest in the mill least affected by mountain pine beetle (Mill A). In all of the mills, the sewered water to the primary treatment contained more extractives in the water phase (dissolved and dispersed) than in the solid phase. This water-born material predominantly consists of fatty and resin acids. This is true also of the solid phase-associated extractives.

The lower amounts of extractives in the feed to the primary clarifier of Mill E, which uses gray-stage wood, is consistent with lower removal of extractives from the pulps of this mill in the

bleach plant and tends to confirm our hypothesis for why the final pulp extractives of this mill are higher.

The analyses of the samples going to secondary treatment show variation. In Mill C, the amounts of extractives are much higher in the secondary treatment sample than they are in the primary clarifier sample, likely due to variability with time in the process. This variability suggests that with the ever-changing wood to the mill, the extractives in the effluent are constantly changing in amount. High extractives in the secondary effluent have been postulated to be a source of foaminess, but results on the foaming properties of sewered waters suggest that the extractives are not the major cause of foaminess (unpublished).

Analyses of the final effluent samples reveal a large reduction in extractives. From the point of view of regulatory toxicity, the resin acids are most important and ideally should have a concentration less than 1 mg/L to avoid a toxicity episode (Kovacs et al. 2004). There is a trend as we proceed from Mill A (10% green stage) to Mill E (gray stage) to higher resin acid concentrations in the final effluent. Although the resin acid concentration in Mill E greatly exceeded the 1 mg/L threshold, it did not result in a toxicity episode at the mill.

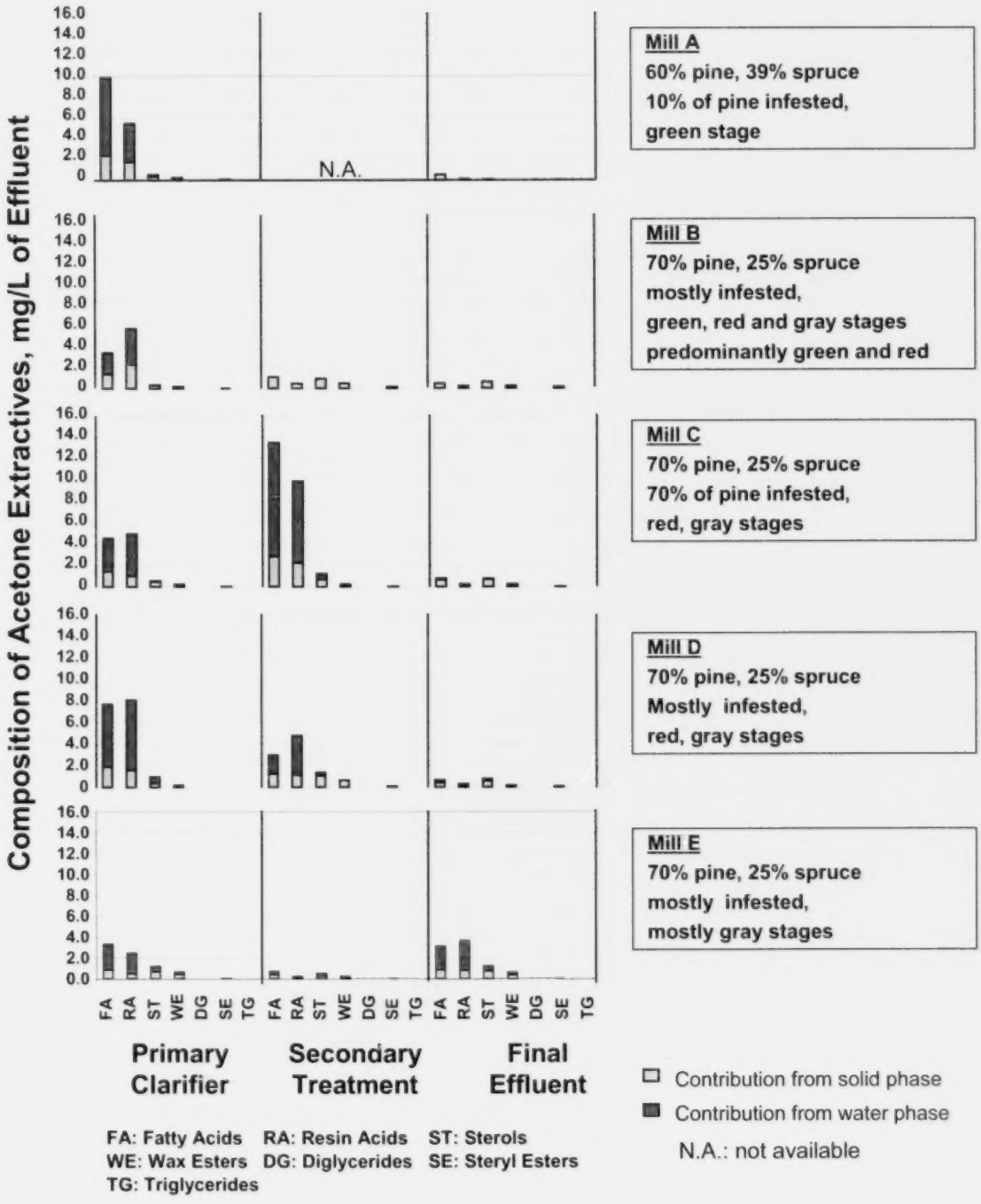

Figure 10. For kraft mills, the acetone extractives of solid and aqueous phases of sewered water to primary clarifier, secondary treatment and final outfall.

3.3.2 TMP and paper mills

The composition of acetone extractives in the sewers from the TMP plant and paper mill and final effluent are presented in Figure 11. It appears that, unlike kraft mills, mechanical pulp and paper mill extractives in the sewers were predominantly bound to the solid phase of the samples: less extractives were dissolved and dispersed in the water phase. The highest extractives were found in the TMP Mill F, which uses green-stage beetle-affected wood. Perhaps this reflects more extractives from the chip-washing operation in wood where extractives under the bark may be highest. The paper mill sewers generally had less fatty and resin acids than the TMP sewer. In almost all of the TMP and paper mill samples, resin acids seemed to predominate in concentration over fatty acids. Good reduction of extractives in the final effluent is evident in all three mills.

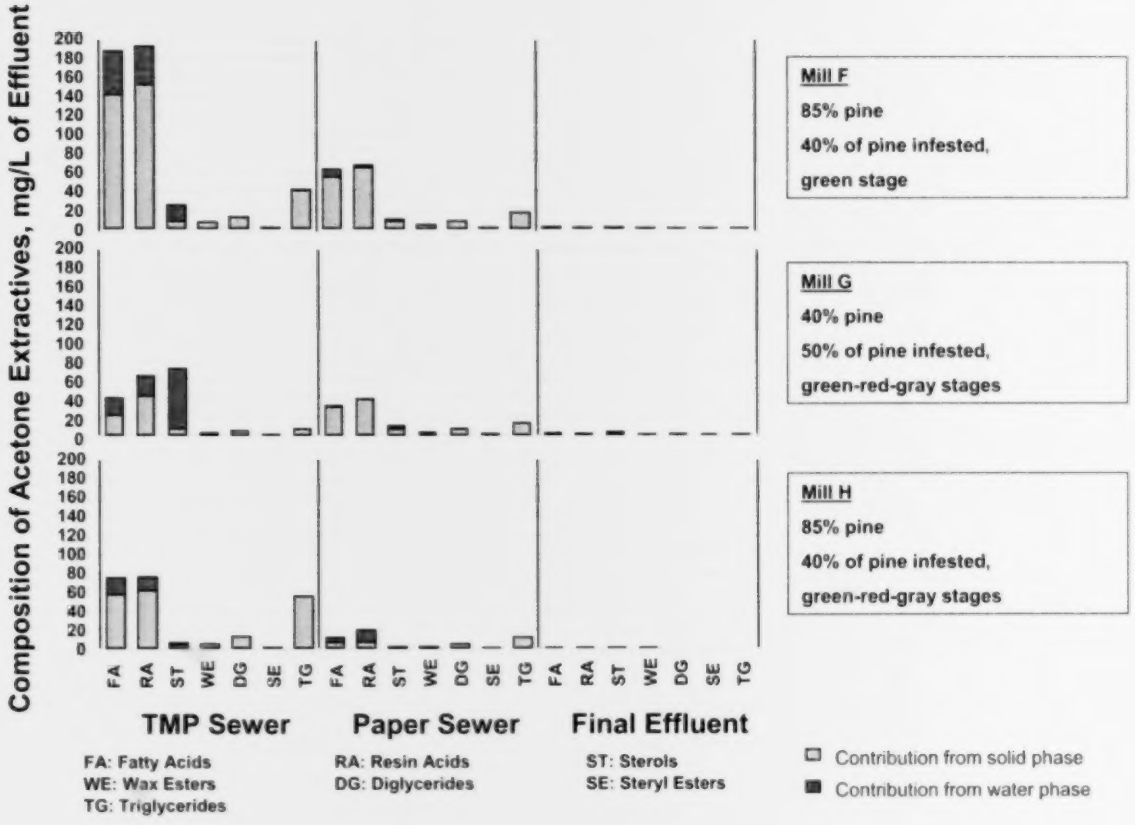

Figure 11. For TMP mills, acetone extractives in solid and aqueous phases of TMP sewer, paper sewer and final effluent.

3.4 Coefficient of friction (COF) in paper samples

Coefficients of friction of the top side of the paper samples containing mechanical pulp are given in Figure 12. For the two newsprint mills, Mills F and G, these coefficients are in the typical range for newsprint (Back 2002; Voosen 1998). From Figure 4, it appears that the extractives in paper from Mill F are twice as high as those in the sample from Mill G. Extractives, especially the fatty acids and glycerides, are a boundary lubricant that can contribute to a substantial loss of COF (Back 2002; Garoff et al. 1999). On the other hand, resin acids have been reported to increase COF (Garoff et al. 1999; Hoyland and Neill 2001). In fact, it was our original intention to try to correlate COF with resin acid content. There are only two newsprint mills represented in Figure 12, and the resin acid content of the extractives at Mill F is a little higher than at Mill G (Figure 7). It would appear that the higher total extractives in Mill F contribute to the lower COF, and this greatly outweighs the possible beneficial effect of higher resin acids in the extractives of Mill F. The COFs all fell within the range reported historically for newsprint (Back 2002; Voosen 1998). The three samples, each from a different paper machine in Mill H, had higher COF values. This is a reflection of the PCC filler, which is known to increase COF, used in the manufacture of paper at Mill H (Back 2002).

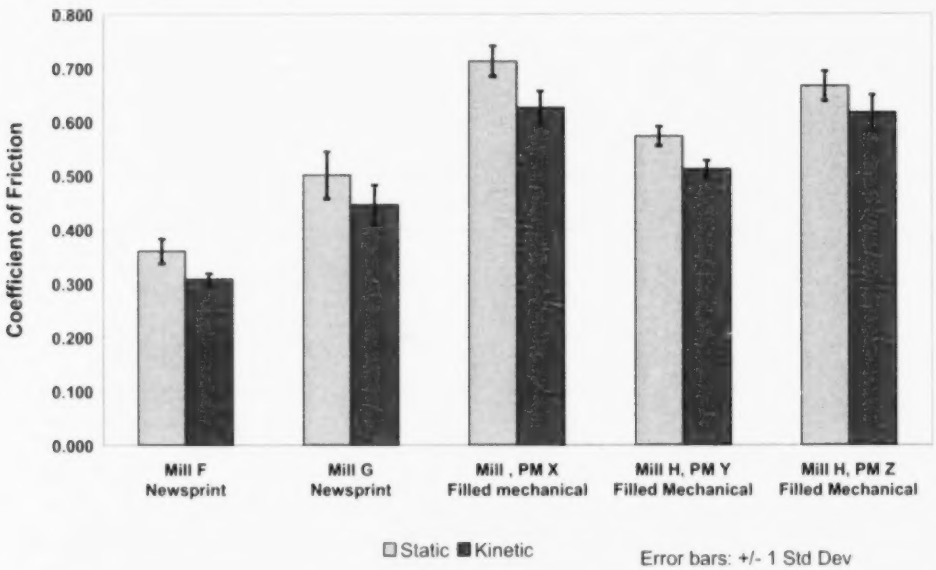

Figure 12. Coefficient of friction (top side) of paper samples from the mills. Mill H was making a filled mechanical grade of paper and not newsprint.
Note: The dark blue bars show results for static friction and the red bars are for kinetic friction.

3.5 Tall oil soap recovery

The soap solubility curves determined for black liquors from Mills C (red-stage beetle-killed wood) and E (gray-stage beetle-affected wood), with and without soap addition, are illustrated in Figures 13 and 14, respectively. The soap solubility curve for black liquors from southern U.S. mills (from Drew and Propst 1981) is also shown on both graphs for comparison. The tall oil measured in the liquors is expressed as soap, assuming a 60% tall oil yield from soap (Uloth et al. 1987). Soap solubility at any given solids concentration for the mills pulping beetle-affected

wood is now significantly higher than that for southern U.S. mills and soap solubility minima (in the 40% liquor solids range) are more than double those for southern U.S. mills. Without soap addition, the curves appear fairly flat, likely because the tall oil soap concentrations in weak black liquor, particularly at Mill C (Table 3), and the prepared lower solids liquors do not exceed the solubility limit. Although soap addition gives many of the measured solubility curves the expected horseshoe shape, it did not significantly affect the measured soap solubility minima. In tests with black liquor from Mill D (Figure 16), soap addition had little impact on the measured solubility curve.

The soap solubility data for black liquor samples from four interior B.C. kraft mills, measured in 1985 (Uloth et al. 1987), are summarized and compared again to that for black liquors from southern U.S. kraft mills in Figure 15. (Mills F and G, in this case, are not the TMP mills of the current study, but are kraft mills from the referenced report.) The soap solubility minima for the B.C. mills ranged from 6 kg to 8.5 kg of soap per tonne of dry black liquor solids in 1985, slightly higher but comparable to the 5 kg per tonne of liquor solids minimum observed for southern U.S. mills. Soap solubility was minimized at the B.C. mills (in 1985) when the black liquor solids concentration was in the 25% to 35% solids range, similar again to the behavior observed in southern U.S. mills.

In Figure 16, soap solubility data for black liquor samples from the four interior B.C. kraft mills, and the one Alberta mill (Mill A) measured in the current study, are summarized and compared again to that for black liquors from southern U.S. kraft mills. Figure 17 details the (fitted) soap solubility curves for the four interior B.C. kraft mills, and the one Alberta mill. The soap solubility minima for the B.C. mills now range from 10.2 kg to 12.7 kg of soap per tonne of dry black liquor solids, more than double the 5 kg per tonne of dry liquor solids minimum observed for southern U.S. mills. The soap solubility minimum for the one Alberta mill, with little beetle-affected wood in the mill furnish, was 8.6 kg per tonne of dry black liquor solids. Soap solubility is now minimized at the B.C. mills when the black liquor solids concentration is in the 35% to 49% solids range. In the 20% to 30% solids range, where most B.C. mills try to skim soap, soap solubility ranged from 12 kg to 20 kg per tonne of dry liquor solids. As illustrated in Table 3, the tall oil soap concentrations in the weak black liquor samples from many of these mills (which ranged from 11.6 kg to 32.6 kg of soap/tonne of dry black liquor solids) did not greatly exceed the solubility limit in the 20% to 30% solids concentration range. In these mills, little or no tall oil soap would be expected to be recoverable from the normal skimming vessels, which are the weak black liquor storage tank and evaporator skimmer [operating at 23% to 32% solids (Uloth and Wearing 1988)]. Soap could, however, be expected to accumulate in strong liquor storage tanks, where it could cause operating problems, and lead to unstable recovery boiler operation.

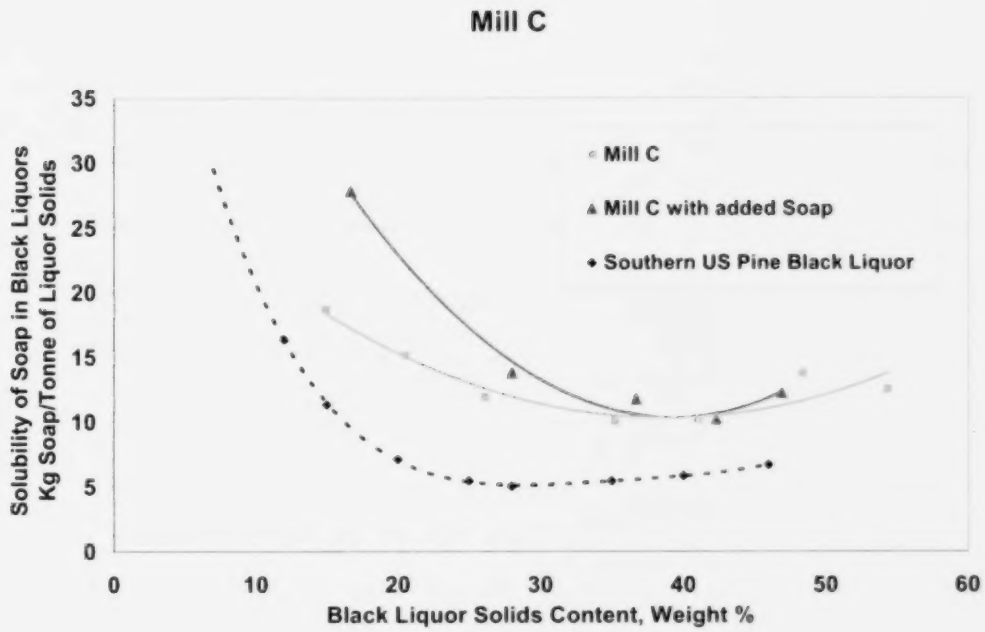

Figure 13. Tall oil soap solubility at 90° C in black liquors from Mill C, a B.C. mill pulping red-stage beetle-killed lodgepole pine wood.

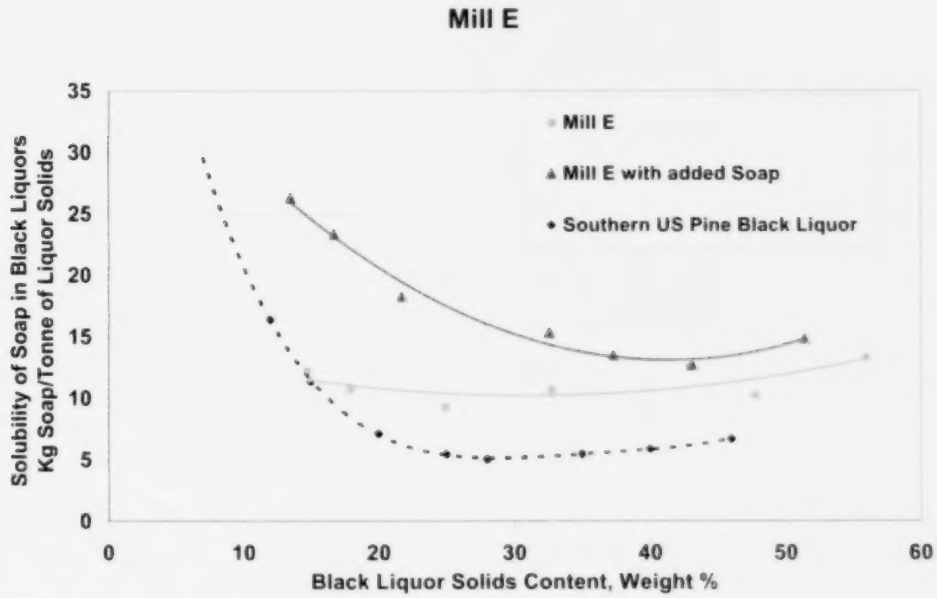

Figure 14. Tall oil soap solubility at 90° C in black liquors from Mill E, a B.C. mill pulping a high percentage of gray-stage beetle-killed lodgepole pine wood.

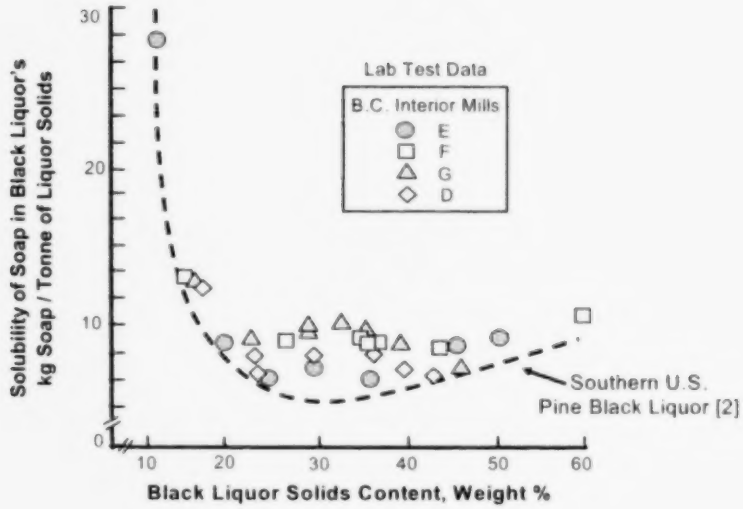

Figure 15. Tall oil soap solubility at 90° C in black liquors taken in 1985–86 from four B.C. kraft mills pulping spruce, pine and fir (Uloth et al. 1987), compared to the soap solubility measured at southern U.S. mills (Drew and Propst 1981).

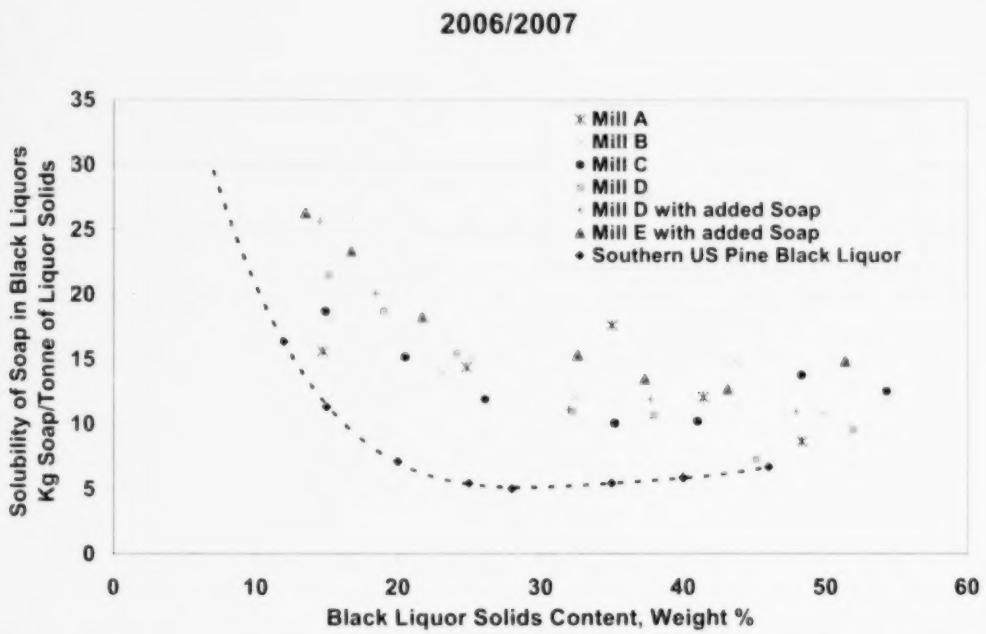

Figure 16. Tall oil soap solubility at 90° C in black liquors taken in 2006 from four B.C. mills pulping red- and gray-stage beetle-killed lodgepole pine and from a mill in Alberta (Mill A) pulping little beetle-affected wood.

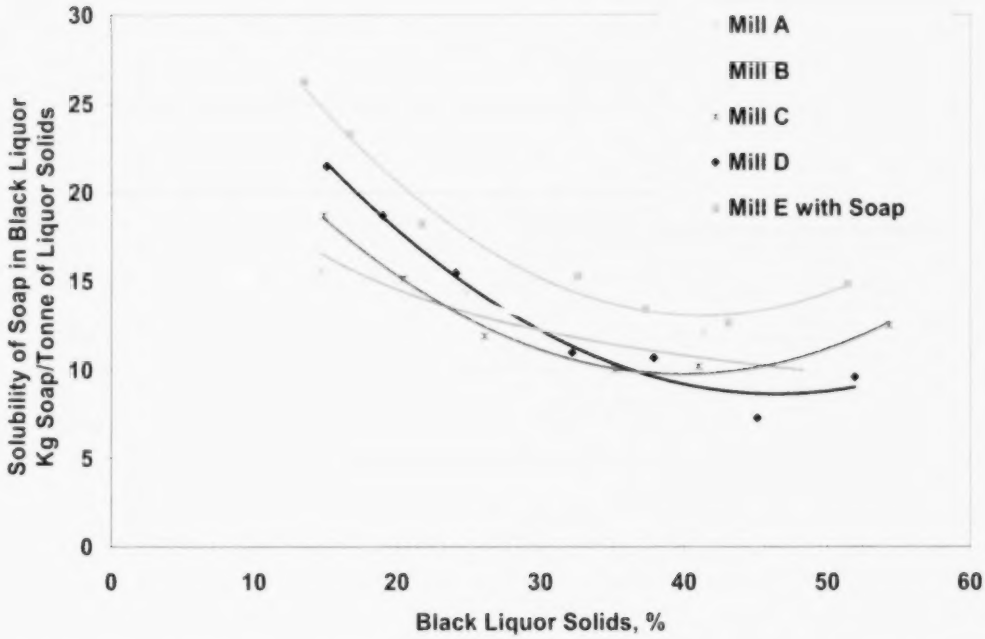

Figure 17. Soap solubility curves at 90° C for the four interior B.C. kraft mills, and one Alberta mill (Mill A).

As summarized in Table 3, the concentrations of soap in the weak black liquor samples from Mills A, B, D and E were similar, ranging from 28.5 kg to 32.6 kg per tonne of dry black liquor solids. The concentration of soap in the weak black liquor from Mill D (11.6 kg/tonne of dry black liquor solids) was much lower, which may explain the effect soap addition had on the soap solubility curve determination (Figure 13). It is interesting to note that the use of beetle-affected wood had little impact on the amount of soap in the weak black liquor at the different mills. Even Mill E, which pulped a large percentage of gray-stage beetle-killed wood, still had lots of soap in its weak black liquor and a loss of soap between the weak and strong black liquor tanks, although the mill reports that it is no longer able to recover appreciable amounts of soap from the normal skim points.

As summarized in Table 3, the concentrations of soap in the strong black liquor samples from these mills ranged from 5.2 kg to 12.5 kg per tonne of dry black liquor solids. Note that the soap concentration in the black liquor at Mill A declines from 28.5 kg per tonne of dry black liquor solids in the weak black liquor to 12.5 kg per tonne of dry black liquor solids in the strong black liquor in spite of the fact that the mill does not actively recover soap. While Mill A operates mixers in the weak and strong black liquor storage tanks to try to keep the soap dispersed, the observed drop indicates that soap is likely accumulating in the mill's storage tanks.

Table 3. Soap content and measured solubility minimums for the black liquors received from the four B.C. mills and one Alberta kraft mill.

Mill description	Sampling Date (2006)	Residual effective alkali in WBL*	Soap in weak black liquor , kg/t of BLS	Soap in strong black liquor, kg/t of BLS	Soap solubility minimum at 90°C, kg soap/t of BLS	Liquor solids concentration at which soap solubility was minimized, %
A - an Alberta mill pulping little beetle-affected wood	July 6	3.8 % (7.1 g/L)	28.5	12.5	8.6	45 - 49
B – a B.C. mill pulping green- and red-stage beetle-affected wood	Apr. 26	10.0% (18.8 g/L)	32.6	5.2	10.8	44 – 48
C – a B.C. mill pulping green- and red-stage beetle-affected wood	Nov. 29	4.41% (8.3 g/L)	11.6	9.3	10.2	35 - 43
D – a B.C. mill pulping red- and gray-stage beetle-killed wood	Oct. 1	5.4% (10.1 g/L)	28.5	8.5	11.1	40 - 44
E – a B.C. mill pulping a high percentage of gray-stage beetle-killed wood	March 3	4.6% (g/L)	29.3	11.3	12.7	40 - 43

* Residual effective alkali expressed as a percent on dry black liquor solids and in grams per litre as Na_2O for 17% to 20% solids weak black liquor

WBL: weak black liquor; BLS: black liquor solids.

For Mills B and D, the concentration of soap in the skimmed strong black liquor was well below the measured solubility limit. This could be due to the fact that all of the liquor samples were taken on the same day and not time staggered. Tests around soap skimmers have shown dramatic variations in liquor soap content over periods as short as 3 hours (Uloth and Wearing 1988). Variations in the liquor residual effective alkali content and the soap resin and fatty acid ratio have also been found to dramatically affect soap solubility (Uloth et al. 1987). Mill data taken around the time of sampling in each mill showed that residual effective alkali concentrations in the weak black liquor often varied by at least 50% from day to day. Although the soaps added to three of the sets of black liquor samples to determine soap solubility curves were taken at the same time as the black liquor samples, this soap could well have had a different composition than the soap in the black liquor samples. The effect of the observed variations in black liquor residual effective alkali content and in soap composition were examined to see if they might explain the observed increases in tall oil soap solubility between 1985 and 2006.

Figure 18 illustrates the effect of both the soap fatty acid/resin acid ratio and black liquor residual effective alkali content on tall oil soap solubility, as found in earlier studies at Canadian mills (Uloth et al. 1987). Mills B, D and E participated in both the 1985 and 2006 studies. These mills are labeled consistently in all of the figures in this report. Note that soap solubility for many of these mills was minimized at solids concentrations in the 32 to 44% range even in 1985. For soaps with a fatty acid/resin acid (FA/RA) ratio between 1.5 and 1.9, soap solubility was doubled if the residual effective alkali (REA) content of digester extraction liquor at 17% to 20% solids concentration was reduced from 10 g/L to 6 g/L as Na_2O (i.e. from about 5.3% to 3.2% REA on dry black liquor solids). As the FA/RA ratio in the soap increased, the minimum soap solubility,

and the REA concentration needed to minimize soap solubility, decreased.

Using the weak black liquor residual effective alkali analyses and soap resin and fatty acid analyses for the liquor and soap samples used in the current solubility tests, the soap solubility minima from the current study were plotted as a function of the liquor residual effective alkali content. The results, summarized in Figure 19, indicate clearly that the observed changes in tall oil soap solubility are largely explained by the observed changes in the soap fatty acid to resin acid ratio. The lower FA/RA ratio in the soap produced from pulping beetle-affected wood results in much higher soap solubility, reducing the recovery potential. The observed increases in soap solubility in the 20% to 30% solids concentration range, and in the solids concentration required to minimize soap solubility (see Table 3), also reduce the effectiveness of existing skimming equipment. Note in Figure 19 that the soap solubility in the Alberta mill (Mill A) still falls very close to the curve determined for soaps with a fatty acid/resin acid ratio of 1.49 to 1.86. While we did not have a soap sample from this mill to check and verify the soap FA/RA ratio, the fatty acid/resin acid ratio for extractives left in brownstock pulp samples from the #2 washer, pre oxygen delignification washer and post oxygen stage wash press, and in the effluent to the aerated stabilization basin, averaged 1.56. Mill A pulps a lot of jack pine and little beetle-affected lodgepole pine. Jack pine contains higher levels of extractives, particularly resin acids, than sound lodgepole pine (Uloth et al. 1987). The slightly lower soap solubility observed at Mill A in the current tests is likely a consequence of a higher fatty acid/resin acid ratio. However, compared to B.C. mills that pulp sound lodgepole pine (Uloth et al. 1987), the soap solubility for mill A lies at the higher end of the observed range, likely due to the higher resin acid content of jack pine.

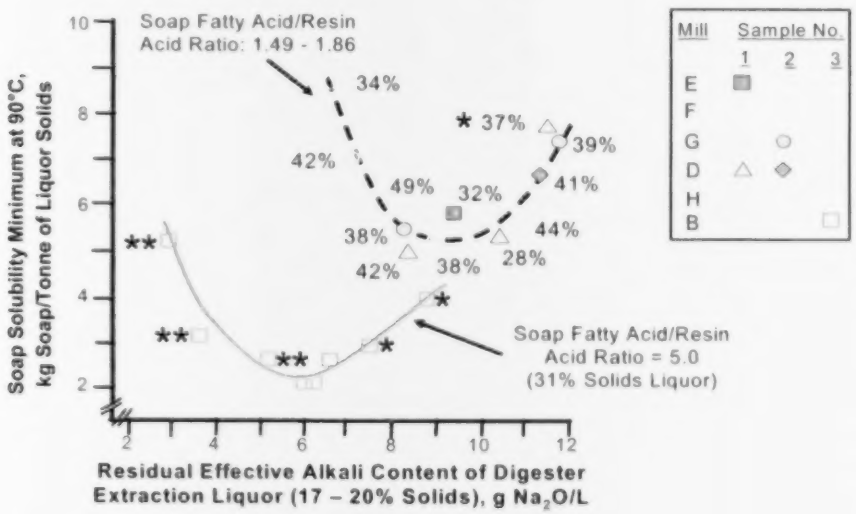

Figure 18. The effect of tall oil soap composition and black liquor residual effective alkali content on tall oil soap solubility minima at 90° C (Uloth et al. 1987). The numbers beside the curve for a soap fatty acid/resin acid ratio of 1.49 to 1.86 indicate the solids concentration at which soap solubility was minimized. * and ** on the second curve indicate that NaOH or sulfuric acid were added to the original liquor.

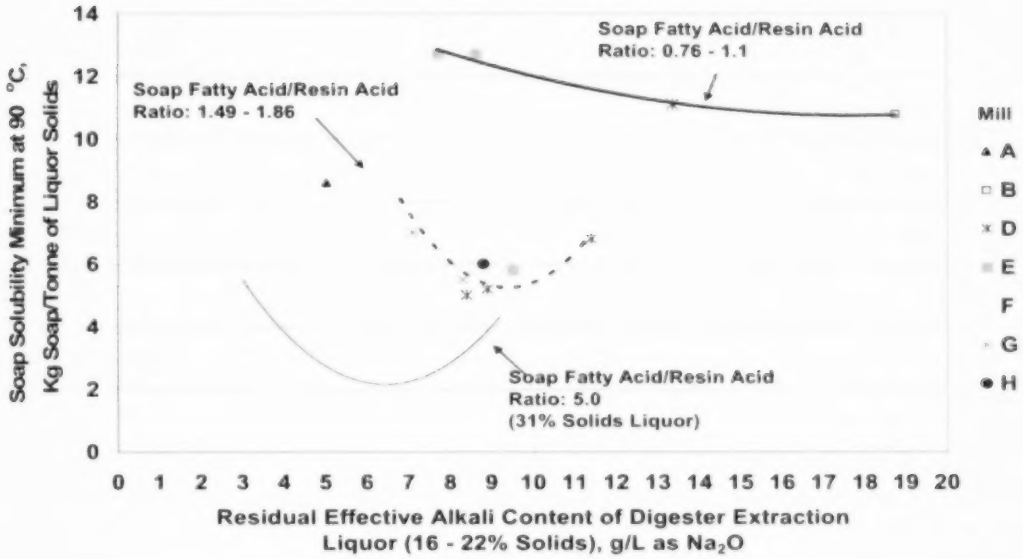

Figure 19. The effect of tall oil soap composition and black liquor residual effective alkali content on tall oil soap solubility minima at 90°C. Mills B, D and E participated in both the 1985 (Uloth et al, 1987) and current studies so soap solubility data for these mills was obtained for different soap fatty acid/resin acid ratios.

The drop in the fatty acid/resin acid ratio for mills pulping beetle-affected wood is a consequence of both the trees' response to beetle attack and the subsequent infection of the trees by fungi vectored by the beetle. When the tree is infected, preformed oleoresin from the damaged resin canals flows out to the site of the attack. This is followed by a secondary resinosis, in which live parenchyma cells around the site of attack produce resinous compounds, including resin acids. Although not all trees produce the secondary response, this reaction will increase the resin acid concentration in affected trees and lower the fatty acid/resin acid ratio in the soap subsequently produced from that wood in the kraft mill. When secondary resinosis is not successful in preventing the establishment of beetles and fungi, the tree will be colonized and soon dies. At the time of attack, it can be assumed that the extractives content of the wood increases due to secondary resinosis. After the tree dies, consumption of cell contents (including extractives) by fungi may lead to a decrease in extractives. Recent studies indicate that after tree death, fungi use mostly sterols, steryl esters, triglycerides, diglycerides and shorter chain fatty acids, which further lowers the fatty acid/resin acid ratio of the soap subsequently produced in the kraft mill using beetle-affected wood. In addition, extractives content is reduced by enzymes in the parenchyma cells, and by oxidation and evaporation. As illustrated in Figure 19, the change in fatty acid/resin acid ratios can dramatically affect tall oil soap solubility and recovery efficiency.

3.6 Seasonal variations in soap composition

Samples of the soap skimmed in each of the four B.C. kraft mills were also taken each month and forwarded to our laboratory. The Alberta mill did not actively recover soap and, thus, was unable to provide us with such monthly samples. Results of the fatty acid and resin acid analyses on the tall oil produced from the monthly soap samples, from March to December 2006, are summarized in Figure 20. In Figure 21, the fatty acid content of tall oil produced from soap samples taken from each mill are shown as a function of the product tall oil acid number. Soap from Mills B and C, which pulped green- and red-stage beetle-affected wood, generally produced tall oils with the highest acid numbers, fatty acid content and fatty acid/resin acid ratio. The fatty acid/resin acid ratios for tall oil produced using the soaps from Mills B and C, as summarized in Figure 20, generally ranged from 1.03 to 1.28, still well below the 1.49 to 1.86 range seen 20 years ago. Tall oil produced using the soaps from Mill D and particularly Mill E had the lowest acid numbers, fatty acid contents and fatty acid/resin acid ratios. As illustrated in Figure 20, the fatty acid/resin acid ratio for tall oil produced using soap from Mill E ranged from 0.72 to 1.06. Mills D and E have reported more chemical recovery system operating problems, many of which could be attributed to higher concentrations of soap in the fired liquor.

The acid number is a measure of the free fatty and resin acids in tall oil, widely used as an indication of quality and value to fractionators. As illustrated in Figure 21, the higher the fatty acid content, the higher the tall oil acid number. As the tall oil acid number drops below 135, tall oil separation time requirements increase, and tall oil plant throughput is decreased (Uloth et al. 1994). Acid numbers for tall oil produced at B.C. mills in the late 1970s ranged from 120 to 142 (Byzyna and Hutton 1979); they currently range from 106 to 133, indicating that area tall oil plants are likely to encounter greater difficulty in processing recovered soap. Tall oil production at mills pulping beetle-affected wood could drop due to both higher soap solubility in black liquor and lower-quality (acid number) soap.

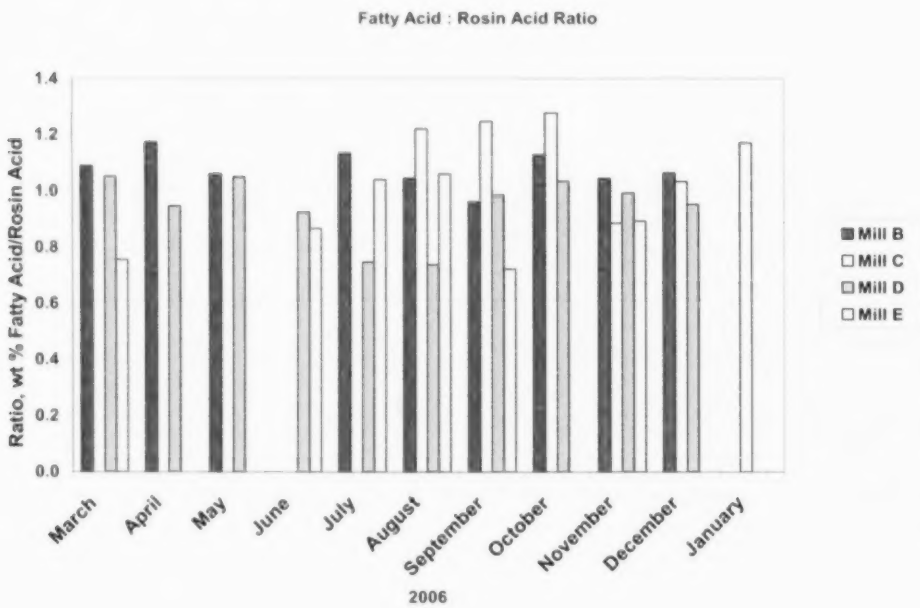

Figure 20. The fatty acid/resin acid ratios for tall oils produced from monthly soap samples taken from four B.C. kraft mills pulping various proportions of green-, red- and gray-stage beetle-affected wood.

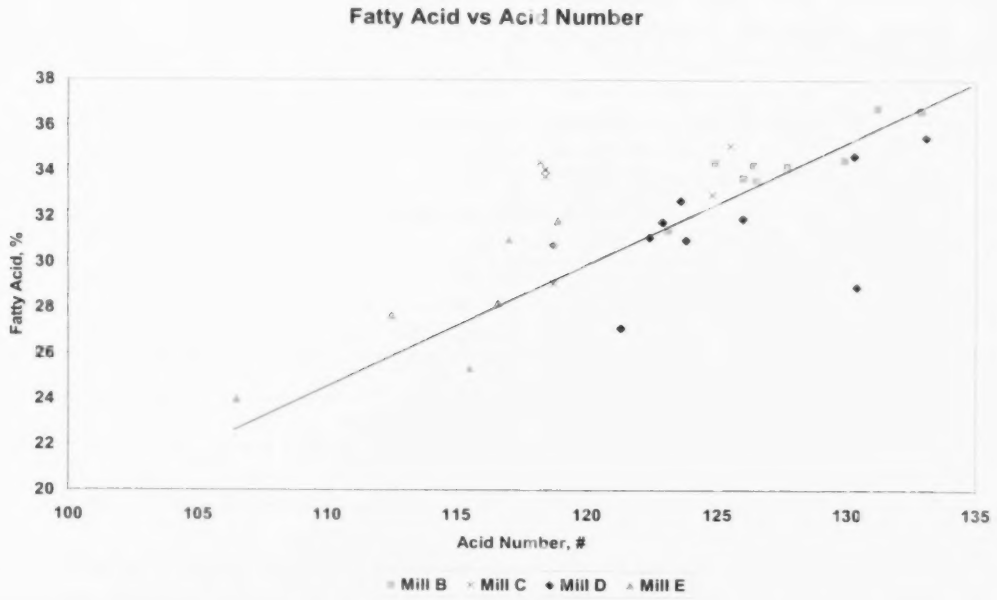

Figure 21. The fatty acid content of tall oil produced from monthly soap samples taken from four B.C. kraft mills as a function of the tall oil acid number.

In processing the monthly soap samples, one additional, potentially important phenomenon was noted. The soap samples received from Mill C in November and Mill E in October and November were observed to sit below a layer of black liquor. As soap is less dense than black liquor (Drew and Propst 1981; Foran 1992; Uloth and Wearing 1988), soap is normally skimmed from the surface of black liquor storage tanks and skimmers. It is rare to see soap that "sinks" unless it is contaminated by a large amount of fibre. Each of these soap samples was reheated to 90° C. Black liquor sank to the bottom of the bottle containing the heated soap sample from Mill C (which produced tall oil with a FA/RA ratio = 0.88). The heated soap samples from Mill E formed a thick black liquid, with no distinct separation between any soap and black liquor layers. When cooled, the lighter brown soap again sat at the bottom of the sample bottle. The black liquor was decanted from the November Mill E soap sample (which also produced a tall oil with a FA/RA ratio = 0.88). We could not get a true soap layer off the October soap sample and could not use the sample to produce tall oil due to the high concentrations of entrained black liquor.

Further investigation unearthed a study (Pearl et al. 1976) that may explain our laboratory observations and the observed reduction in soap recovery at many mills pulping beetle-affected wood. Studies at the Institute of Paper Chemistry investigated the solubility of synthetic mixtures of the soaps of refined tall oil fatty (TOFA) and resin (TORA) acids in 1 Normal sodium hydroxide, diluted black liquor and skimmed partially concentrated black liquor. Similar to Uloth et al. (1987) and the current study, they found that soap solubility increased as the resin acid content of the soap increased. They also found that, instead of forming a distinctive soap layer on top of the dilute (21% solids) black liquor, the soap formed a sludge which sank to the bottom of the flask when the fatty acid/resin acid ratios dropped below 1.0. The authors credited this behavior to increased soap density and suggested air addition as one potential means to increase soap recovery. Although these experiments were conducted with pure fatty and resin acids, rather than soap, together with our observations on the monthly soap samples, they suggest that poor

soap recovery in many mills could be due to higher soap density and a reduced tendency to "float" off in storage vessels and skimmers. Calculations by Uloth and Wearing (1988) have already demonstrated the importance of both the density difference and the black liquor viscosity on soap separation efficiency. Additional testing would be required to confirm the proposed effects of the fatty acid/resin acid ratio on soap density and to examine ways to improve recovery of high-resin acid soaps, such as those produced from pulping mountain pine beetle-affected wood.

3.7 Effect of soap on black liquor properties

Mills that do not separate soap for tall oil production can have high soap content (around 2.5%) in their black liquor. The soap will increase the heating value of the black liquor (see Table 4), which may be advantageous, provided the boiler is not steam limited (Uloth et al. 1987). Other beneficial effects include a reduction in chemical make-up, increased bed temperature and increased reduction efficiency (Morgan 1979). However, if soap is not removed, it can adversely affect the washing and recovery operations. Burkeite ($2Na_2SO_4$-Na_2CO_3) and $CaCO_3$ scaling in the evaporators are greatly accelerated in the presence of soap (Uloth and Wong 1986; Frederick and Grace 1977). Soap is normally skimmed in one or two stages from black liquor prior to and during evaporation (Uloth et al. 1987). In the recovery boilers, blackouts have been associated with the entry of slugs of soap containing weak black liquor (Milanova et al. 1985). To avoid these problems, soap should be recovered (skimmed) and, if the separated soap is to be burnt in the recovery boiler or particularly in the power boiler or lime kiln, it should be first acidified to crude tall oil (Tikka et al. 2002). Many mills that do not have an acidification plant have difficulty selling their soap or even giving it away. These mills often add soap to the strong or as-fired black liquor, even though this may reduce liquor throughput in the recovery boiler. In this case, it is important to insure a homogenized mixture and a uniform flow to prevent unstable recovery boiler operation.

The viscosity of tall oil soap varies widely, depending on soap composition and entrained black liquor content. However, viscosity of soap is often an order of magnitude higher than that of black liquor (Drew and Propst 1981).

To study the effect of soap on black liquor properties, a sample of as-fired black liquor and a sample of soap were obtained from a B.C. kraft mill (Mill H) pulping a mixture of spruce, pine and fir (SPF). Pulping at this mill is done in a continuous digester to a kappa number between 35 and 40. No spent acid (sodium sesquisulphate) was added to the black liquor for about 7 days prior to black liquor sampling. The soap is collected primarily from the weak black liquor storage tank, but some is taken from several intermediate and strong black liquor tanks. The collected soap is sent to a retention tank to further separate black liquor. The separated soap at this particular facility is then processed for tall oil production. More black liquor was removed from the as-received soap sample in our laboratories before it was analyzed and used for spiking black liquor samples. The analysis results for the as-fired black liquor and the soap samples, on a dry solids basis, are shown in Table 4.

Table 4. Chemical analyses results for the as-fired black liquor and soap

Sample	Solids %	Lignin %	Soap %	S^{-2} %	Na %	Ca %	HHV BTU/lb	Org./ Inorg.	Swelling mL/g	pH
As-fired BL	73.0	31.8	1.1	5.45	17.7	0.04	6017	1.7	31.7	14.0
Soap	62.8	14.5	68.5	0.3	5.6	0.32	15139	5.6	–	13.2

The as-fired black liquor was spiked with soap to cover a concentration range from 1.1 (the original soap content of the liquor) to 5.7% soap (on dried solids). The percentage of solids in

each of the spiked liquors were adjusted, so that all of the samples had the same percent solids (70.2%). The samples were well mixed and then transferred to the Haake pressurized viscometer. The viscosities were measured over a temperature range of 115° C to 130° C at a constant shear rate of 250 s^{-1}.

Figure 22 shows the effect of soap content on the viscosity of black liquor. Although the addition of soap increased the viscosity of the black liquor, increasing the firing temperature by a few degrees was found to reduce the viscosity to baseline levels.

The only other reported work (Soderhjelm and Sagfors 1994) on the effect of soap on the viscosity of black liquor concluded that soap content (0.2% to 2.3%) has no effect on black liquor viscosity. Their results, however, were obtained by extracting wood chips and by adding tall oil soap back into the chips prior to pulping. In our experiments, we simulated a mill case where the skimmed soap is added back into the liquor burnt in the recovery boiler.

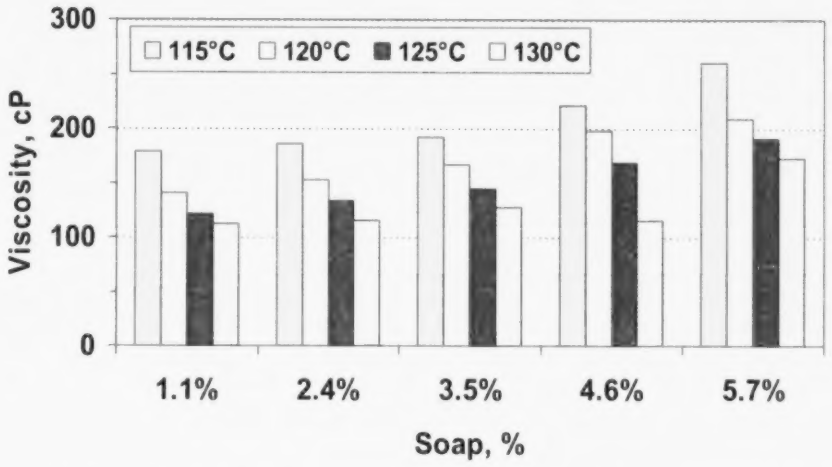

Figure 22. The effect of increasing soap content on the viscosity of 70.2% solids black liquor at different temperatures for black liquor from a B.C. mill pulping spruce, pine and fir (SPF).

Another potential factor that might result in increased black liquor viscosity with high levels of soap addition could be the metal content of the soap. The calcium content of the soap sample was about an order of magnitude higher than that in the corresponding black liquor (Table 4). High levels of calcium and magnesium have been reported to promote the flocculation of lignin and cause increases in black liquor viscosity (Ledung and Ulmgren 2000).

In Figure 22, the percent soap is based on dry solids. Many mills, however, use percent by volume when setting the soap addition rate. Table 5 compares percent soap on dry solids vs. percent volumetric for the black liquor and soap used in this study. The practical range when adding skimmed soap back into black liquor for firing in a recovery boiler is about 2% soap on dry solids or about 5% by volume.

The addition of soap reduced the swelling propensity of the black liquor as expected (Milanova et al. 1985; Alen 1998); the reduction in swelling versus the increase in the soap content was approximately linear (Table 5). The addition of soap also increased the liquor heating value. The resulting heating values agreed well with the calculated values.

Table 5. Comparison of percent soap on dry liquor solids versus vs. percent volumetric and swelling and heating values

% Soap solids	1.1	2.4	3.5	4.6	5.7
% Soap volume	2.9	6.1	8.9	11.7	14.5
Swelling index, mL/g	36.9	31.2	23.0	20.7	19.5
HHV (higher heating value), BTU/lb	6228	6370	6561	6638	6734

Some mills fire soap with the black liquor, because they do not have an acidification plant and cannot dispose of the separated soap. Many of the mills pulping beetle-affected wood find that they are no longer able to effectively skim soap from the black liquor, that the soap content of their fired liquor is increasing, or that periodic spikes in the fired liquor soap content give them operating problems, including issues with boiler plugging. During recovery boiler optimization tests in at least two mills, Paprican ran tests to evaluate the impact of soap addition on boiler operation. These tests indicated that the addition of soap to the fired liquor erroneously lowers the liquor solids concentrations measured by the mill's refractometers. This erroneous reading increased the liquor firing rate slightly (by ~ 1%) at one mill that ran the recovery boiler at a fixed black liquor solids firing rate. The higher firing rate and higher liquor calorific value (see Table 5) resulting from soap addition increased the boiler steaming rates at a fixed solids loading significantly (by ~ 6.3%). Vakkilainen and Pekkanen (2002) reported that although several Finnish mills fire soap mixed with black liquor with good success, their refractometers have to be recalibrated as soap addition can change the refractive index resulting in erroneous solids estimates from the on-line refractometers (1.0% to 2.5% differences from the actual). Several of these Finnish mills also encountered unexpected problems with high SO_2 emissions when burning tall oil soap. The observed impacts are consistent with the changes in liquor properties observed during the studies summarized here. Tall oil soap addition increases black liquor viscosity producing larger liquor droplets at constant firing conditions (i.e., with constant gun pressures and firing liquor temperatures). Tall oil soap addition also causes black liquor droplets to swell less during pyrolysis and to burn slower (Milanova at al. 1985). These slow-burning (lower surface area) larger droplets may reach the bed before drying and cause blackouts or smelt-water contact. Vakkilainen and Pekkanan (2002) and Uloth et al. (2007) reported that soap-laden liquor needs to be fired with a lower average droplet size than soap-free liquor. They recommended that firing liquor temperature, or liquor gun pressure, be increased slightly when adding soap to the fired black liquor.

Paprican's tests in two recovery boilers indicate, however, that without operating modifications (i.e., keeping the gun pressures, liquor firing temperature and combustion air splits constant), high concentrations of soap in the fired liquor lower the char bed temperature and increase burning in flight and carryover levels in the upper boiler. Because soap does not dissolve completely in black liquor and because soap has a much higher viscosity than black liquor, we believe that soap firing increases the droplet-size distribution, creating more fine and coarse droplets at a given set of firing conditions. When carryover and boiler plugging are the primary concerns [as opposed to total reduced sulfur (TRS) and SO_2 emissions], liquor gun angles or firing temperature may need to be lowered to reduce carryover and direct more of the liquor to the char bed. When the liquor firing temperature or gun angles are lowered, operating personnel may need to increase the

primary air flow to effectively burn the added liquor reaching the bed and avoid low bed temperatures, which may increase TRS emissions.

The reactions necessary to combat operating problems caused by high soap content in the fired black liquor are very likely to be boiler specific and to depend on the particular boiler's operating conditions, major operating problems (TRS or SO_2 emissions or boiler plugging) and limitations.

4 Conclusions

4.1 Extractives in mills

4.1.1 Kraft mills

After unbleached washing, use of mountain pine beetle-affected wood in the green and red stages did not cause a change in the normal amount of extractives across the mill greater than the normal variability due to changes in incoming wood. With wood in the gray stage, however, preliminary results suggest that the amount of extractives in the final pulp can be significantly higher; e.g., double. For most customers, this higher extractives level, e.g., from 0.04% to 0.08%, will not make a significant difference. Nevertheless, many kraft mills do sell pulp to some extractives-sensitive customers that may be affected if their papermaking process is already operating with conditions close to a pitch problem. Hence, the greater extractives in kraft pulp made from gray-stage beetle-affected wood deserves further research, both to further substantiate our observation and to devise ways to decrease extractives in the final pulp.

As for the chemical composition of the extractives, for mills using green- and red-stage wood, we observed nothing unusual in the composition of the extractives after brownstock washing. In the mill pulping mostly gray-stage wood, we observed significantly higher amounts of sterols and wax esters (often referred to as unsaponifiables) in pulps starting at the Eop stage and going through to the final pulp. These unsaponifiables are less easily washed from kraft pulp (Allen and Lapointe 2003), and this may account for the higher extractives content in the final pulp. As already stated, most customers will not be affected by an elevated level of unsaponifiables; however, these unsaponifiables will be partially dispersed during repulping and refining at customer paper mills and present some potential to cause or exacerbate pitch problems.

To understand these findings, it is important to keep in mind that beetle attack occurs in the cambium of lodgepole pine trees. This is the layer between the wood and bark. Hence, the trees' efforts to pitch out beetles result in exudation of canal resin consisting largely of resin acids and terpenes into the bore holes and tunnels. During subsequent barking and chipping, much of this canal resin is lost from the chips. The blue-stain fungi that are vectored by the beetles, on the other hand, do penetrate the wood, and one might expect a reaction from the tree to this process, such as the generation of canal resin. In any event, the excess resin seems to be eliminated in the digester and brownstock washing. For gray-stage wood, the resin to fatty acid ratio is higher in the digester. This results in greater solubility of fatty and resin acids in the black liquor, poorer soap separation, and better removal of fatty and resin acids in brownstock washing. As gray-stage pulps contain less fatty and resin acids after unbleached washing, it is possible that there will be less solubilization of the unsaponifiables in subsequent alkaline washing; this may account for gray-stage pulps having higher unsaponifiable content.

For mills processing green- and red-stage beetle-affected wood, there will probably be a greater dependence on brownstock washing to remove any excess extractives.

4.1.2 TMP and paper mills

Use of beetle-affected wood did not cause significant change in the normal amounts of extractives across the mill in going from a mill using 40% beetle-affected wood in the green stage to mills using 40% beetle-affected in green, red, and gray stages. In addition, there was nothing unusual in the composition of the extractives.

4.2 Pitch control in mills

4.2.1 Kraft mills

Although beetle-affected wood in green and red stages may contain higher amounts of extractives, as demonstrated by improved soap skimming, the extra extractives are mostly in the form of resin acids, and these are easily removed in brownstock washing. Resin acids usually do not cause pitch problems in kraft mills due to their greater solubility compared to that of fatty acids. As a result, after brownstock washing, the extractives in pulp from green- and red-stage beetle-affected wood exhibit normal amounts of resin, and the composition is unchanged from that of non-beetle-affected wood. It follows that many mills are likely able to tolerate mountain pine beetle-affected wood without changes in pitch control program. Nevertheless, if the mill is facing an influx of green- and red-stage wood, common sense dictates that some tightening of pitch control practices, especially in the unbleached part of the mill, would be wise (Allen 2000a; 2000b).

One kraft mill that encountered a severe pitch problem when processing green- and red-stage beetle wood had problems in the brownstock washing area. The problems appeared to begin when they used very finely divided purchased lime in the recausticization plant. This lime was not well removed from the cooking liquor, because of its smaller particle size, and it carried over with the pulp into brownstock washing. The result was rapid and massive deposition on the washers, so that the washer face wires plugged and quickly rendered the washers inoperable. The result was several days of lost production (and consequent loss of millions of dollars) while the unbleached part of the mill was cleaned up. Although not predictable, due to the unusual nature of this problem (we have not encountered it before), the interaction of calcium carbonate particles with fatty and resin acids and their calcium soaps is well documented (Douek and Allen 1983). Good white liquor clarification is a keystone in kraft mill pitch control practices. It would appear that the combination of high resin and fatty acid content of the unbleached pulp with poor white liquor clarification resulted in a particularly severe problem.

It follows from this experience that kraft mills processing mountain pine beetle-affected wood are reliant on brownstock washing to remove fatty and resin acids. Consequently, good pitch control practices in this area, including avoiding bypassing of brownstock washers, good white liquor clarification, high temperature of initial brownstock washing, and judicious use of defoamers, are very important. (The mill in question was overusing brownstock defoamer.)

Personnel in kraft mills using mostly gray-stage beetle wood should also be aware that the extractives in their final product will likely be elevated by as much of a factor of 2. This may result in more pitch problems for certain customer mills.

4.2.2 TMP and paper mills

TMP plants pulping green- and red-stage beetle-affected wood may find they need to use a pitch dispersant to prevent plugging of grooves in refiner plates. At the time of sampling, this was the practice in both Mills G and H.

Although our extractives measurements in a limited number of mills suggested that amounts and composition of extractives are not greatly affected by use of beetle-affected wood, common sense suggests that some tightening of pitch control practices in TMP plants and paper mills using such wood should be done.

4.3 Friction properties of paper

An increase in the resin acid content of the wood supply should, in theory, cause higher coefficients of friction in wood-containing papers. Our observation was that, within the variation of coefficient of friction (COF) from mill to mill (due to species of wood used, differences in paper surface due to different process conditions, etc.) we found no change in paper COF associated with beetle-affected wood use. That is, the COFs all fell within the range reported

historically for newsprint, and we saw no differences in the two newsprint mills going from largely pre-attack/green-stage fibre to red- and gray-stage fibre. Due to the lack of sufficient samples (only two newsprint mills), this observation must be considered preliminary.

4.4 Effluent treatment

In TMP pulp and paper mills, the effluent treatment plants continued to reduce extractives to almost zero in the final effluent, without any adverse effect from beetle-affected wood in any of the stages of time since attack. In the kraft mill using gray stage infested wood, the resin acid concentration in final effluent was high. This gray stage result requires further confirmation.

4.5 Tall oil soap separation

Soap solubility tests, using black liquor and soap samples from four B.C. mills, as well as one Alberta mill that pulped very little beetle-affected wood, showed that soap solubility is increased when pulping beetle-affected wood. The minimum soap solubility in the B.C. mills increased from 6.0 – 8.5 kg per tonne of dry liquor solids in the mid-1980s to 10.2 kg to 12.7 kg per tonne of dry black liquor solids now. The change in soap solubility is largely a result of changes in the fatty acid (FA) and resin acid (RA) content of the wood, resulting from beetle attack and fungi colonization. The FA/RA ratios in tall oil produced from soap skimmed in the B.C. mills has dropped from a range between 1.49 and 1.86 in the mid- 1980s to a range from 0.72 to 1.28. This has shifted the soap solubility versus black liquor solids curves up and to the right. The solids concentrations at which soap solubility is minimized have increased from 25% to 35% to 35% to 49% as a result of the change in the FA/RA ratio. In the 20% to 30% solids range, where most B.C. mills try to skim soap, soap solubility ranged from 12 kg to 20 kg per tonne of dry liquor solids. The tall oil soap concentrations in the weak black liquor samples from many of these mills (which ranged from 11.6 kg to 32.6 kg of soap/tonne of dry black liquor solids) did not greatly exceed the solubility limit in the 20% to 30% solids concentration range. In these mills, little or no tall oil soap would be expected to be recoverable from the normal skimming vessels—the weak black liquor storage tank and evaporator skimmer (operating at 23% to 32% solids). Soap could, however, be expected to precipitate at higher solids concentrations and accumulate in strong liquor storage tanks, where it could cause operating problems and lead to unstable recovery boiler operation.

The acid number is a measure of the free fatty and resin acids in tall oil, widely used as an indication of quality and value to fractionators. Tests on soap samples taken monthly from the four B.C. mills showed that the higher the fatty acid content, the higher the tall oil acid number. Soap from Mill E, which pulps a large percentage of gray-stage beetle-killed wood, had very low fatty acid content and very low acid numbers. As the tall oil acid number drops below 135, tall oil separation time requirements increase greatly, and tall oil plant throughput is decreased. Acid numbers for tall oil produced at B.C. mills in the late 1970s ranged from 120 to 142; acid numbers now range from 106 to 133. This change indicates that area tall oil plants are likely to encounter greater difficulty in processing recovered soap. Tall oil production at mills pulping beetle-affected wood could drop substantially due to both higher soap solubility in black liquor and lower-quality (acid number) soap.

In addition, soap separation and soap quality were observed to be impaired when the fatty acid/resin acid ratios in the monthly soap samples dropped below about 0.9. Earlier studies using pure tall oil fatty acids (TOFA) and tall oil rosin acids (TORA) indicate that, instead of forming a distinctive soap layer on top of the black liquor, soap will form a sludge which sinks to the bottom of storage vessels when the fatty acid/resin acid ratio drops below 1.0. This behavior, observed with the monthly soap samples from at least two B.C. mills, was earlier attributed to increased soap density; air addition was suggested as one potential means to increase soap recovery. Our observations suggest that poor soap recovery in many mills could be due to higher soap density and a reduced tendency to "float" off in storage vessels and skimmers. Earlier

calculations have demonstrated the importance of both the density difference and the black liquor viscosity on soap separation efficiency. Additional testing would be required to confirm the proposed effects of the fatty acid/resin acid ratio on soap density and to examine ways to improve the recovery of high resin acid soaps, such as those from pulping mountain pine beetle-affected wood.

Increasing soap concentrations in fired black liquor were found to increase the viscosity and heating value of the black liquor. Although increasing the firing temperature by a few degrees was found to reduce the viscosity to baseline levels, the soap decreased the swelling propensity of the liquors, making them more difficult to burn. Tests in two recovery boilers indicate that, without operating modifications (i.e., keeping the gun pressures, liquor firing temperature and combustion air splits constant), high concentrations of soap in the fired liquor lower the char bed temperature and increase burning in flight and carryover levels in the upper boiler. Although increasing the liquor firing temperature when burning black liquor with high concentrations of soap has been recommended (Vakkilainen and Pekkanen 2002; Uloth et al. 2007), the reactions necessary to combat operating problems caused by high soap content in the fired black liquor are likely to be boiler specific and to depend on a boiler's operating conditions, major operating problems (TRS or SO_2 emissions or boiler plugging) and limitations.

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6 Literature cited

Alen, R. 1998. Relationship between the Chemical Composition and the Combustion Properties of Black Liquor. *Pages* 185–192 *in* Proceedings of the 1998 International Chemical Recovery Conference, Tampa, FL, vol. 1.

Allen, L.H. 2000a. Pitch Control in Pulp Mills. *Pages* 265–287 *in* Pitch Control, Wood Resin and Deresination. E. Back and L.H. Allen, eds. TAPPI Press, Atlanta.

Allen, L.H. 2000b. Pitch Control in Paper and Board Mills. *Pages* 307–328 *in* Pitch Control, Wood Resin and Deresination. E. Back and L.H. Allen, eds. TAPPI Press, Atlanta.

Allen, L.H.; Lapointe, C.L. 1987. Physical Distribution of Resin in Bleached Kraft Pulp Mills. Pulp Paper Can. 88(12):T483–490.

Allen, L.H.; Lapointe, C.L. 2003. Temperature and pH: Important Variables for Deresination in Kraft Brownstock Washing. Pulp Paper Can. 104 (12):T294–297.

Allen, L.H.; Maine, C.J. 1978. Dispersed Pitch Particle Concentrations in Pulp and Paper Mills. Pulp Paper Can. 79(4):T152–159.

Anonymous, 2006. Coefficients of Static and Dynamic Friction of Uncoated Writing and Printing Paper by Use of the Horizontal Plane Method. TAPPI Test Method T 549 om-06, TAPPI Press, Atlanta.

Back, E.L. 2002. Paper Friction. *Pages* 451–476 *in* Handbook of Physical Testing of Paper, Vol. II. J. Borch; M.B. Lyne; R.E. Mark; C.C. Jr. Habeger, eds. Marcel Dekker, New York, 2nd edition.

Byzyna, L.; Hutton, G. 1979. Seasonal Variations in Soap Quality and Yield. *Pages* 33–44 *in* Soap/Tall Oil Recovery Workshop, Canadian Pulp and Paper Association Technical Section Western Branch, Prince George, B.C.

Crouse, N.E.; Stapley, C.E. 1979. Dregs: Their Cause and Effect. Pulp Paper Can. 80(C):T93–98.

Douek, M.; Allen, L.H. 1980. Calcium Soap Deposition in Kraft Mill Brownstock Systems. Pulp Paper Can. 81(10):T317–T322.

Douek, M.; Allen, L.H. 1983. Adsorption of Soaps on Calcium Carbonate: Significance to Calcium Soap Deposition in Kraft Mill Brownstock Systems. J. Pulp Paper Sci. 9(2):TR48–54.

Drew, J.; Propst. M. 1981. *Tall Oil.* Pulp Chemicals Association, New York. pp. 21–29.

Ekman, R.. 2000. Resin during Storage and in Biological Treatment. *Pages* 185–225 *in* Pitch Control, Wood Resin and Deresination. E.L. Back; L.H. Allen, eds. TAPPI Press, Atlanta.

Ekman, R.; Holmbom, B. 2000. The Chemistry of Wood Resin. *Pages* 37–65 *in* Pitch Control, Wood Resin and Deresination. E.L. Back; L.H. Allen, eds. TAPPI Press, Atlanta.

Foran, D. 1992. Tall Oil Soap Recovery. *Pages* 45–56 *in* Chemical Recovery in the Alkaline Pulping Process. R. P. Green and G. Hough, eds. TAPPI Press, Atlanta.

Frederick, W.J., Jr.; Grace, T.M. 1977. A Study of Evaporator Scaling: Calcium Carbonate Scales", Institute of Paper Chemistry, Project 3234, Progress Report H. pp. 60–61.

Garoff, N.; Jernberg, S.; Nilvebrant, N.-O.; Fellers, C.; Bäckström, M. 1999. The Influence of Wood Extractives on Paper-to-Paper Friction. Nordic Pulp Paper Res. J. 14(4):230–329.

Hoyland, R.W; Neill, M.T. 2001. Factors Affecting the Frictional Properties of Paper: The Effect of Fillers and Rosin Size, Pap. Technol. 42(1):52.

Kovacs, T.; Gibbons, S.; O'Connor, B.; Martel, P.; Paice, M.; Naisch, V.; Voss, R. 2004. Summary of Case Studies Investigating the Causes of Pulp and Paper Mill Effluent Regulatory Toxicity, Water Qual. Res. J. Can., 39(2): 93- 102.

Kubes, G.J. 1983. The Effect of Wood Species on Kraft Recovery Furnace Operation: An Investigation Using Differential Thermal Analysis. *Pages* B19–25 *in* Proceedings of the 69th Annual Meeting of the Canadian Pulp and Paper Association Technical Section, Montreal, P.Q.

Lamy, E. J. 1979. Process Changes Reduce Mill's Concentrator Fouling Problems. Pulp Paper 53(14):92–95.

Ledung, L.; Ulmgren, P. 2000. Viscosity Changes in Black Liquor when Bleach Plant Filtrates

are Added. Nordic Pulp Paper Res. J. 15(4):275–281.
Lenz, B.L. 1977. Effect of Hardwood Black Liquor on Tall Oil Separation. TAPPI 60(5):121–123.
Letonmyaki, N.M.; Selivanova, T.A.; Skvortsova, L.V; Komshilov, N.F. 1964. Bumazhnaya Promyshlennost 39(1):9–11.
Milanova, E.; Dorris, G. 1994. On the Determination of Residual Alkali in Black Liquors. Nordic Pulp Paper Res. J. 9(1):4–9.
Milanova. E.; Kubes, G.J.; Fleming, B.I. 1985. The Swelling of Black Liquor Solids. *Pages* B69–71 *in* Proceedings of the 71st Annual Meeting of the Canadian Pulp and Paper Association Technical Section, Montreal, P.Q.
Morgan, M.C. 1979. The Effect of Soap Recovery on Boiler Capacity. *Pages* 25–37 *in* Proceedings of the Soap/Tall Oil Recovery Workshop, Prince George, B.C. October 3–4, 1979, A Wong, ed. Canadian Pulp and Paper Association.
Norman. H. 1982. The Naval Stores Industry in Canada. *Pages* 8–33 *in* A. Wong, ed., Proceedings of the Second Canadian Soap/Tall Oil Recovery Workshop, Thunder Bay, Ontario. March 31–April 2, 1982. Canadian Pulp and Paper Association.
Nugent, H.M.; Allen L.H.; Bolker, H.I. 1977. Effect of Seasoning on the Acetone Extractives Composition of the Wood from Black Spruce, Jack Pine and Trembling Aspen. Transactions of the Technical Section of the Canadian Pulp and Paper Association 3(4):103–109.
PCA-24. 1977. Method of Estimating Crude Tall Oil in Black Liquor Samples. Analytical Procedures for Tall Oil Products. Pulp Chemicals Association, New York.
PCTM 1. 1996. Method of Determining Acid Number of Tall Oil Using a Potentiometric End Point. Pulp Chemicals Association, Inc., Atlanta, GA.
PCTM 7a. 1996. Content of Tall Oil in Tall Oil Soap. Pulp Chemicals Association, Inc., Atlanta, GA.
PCTM 17. 1996. Method to Determine Rosin Acids in Tall Oil. Pulp Chemicals Association, Inc., Atlanta, GA.
PCTM 20. 1996. Method of Calculating Fatty Acid Content of Tall Oil. Pulp Chemicals Association, Inc., Atlanta, GA.
Pearl, I.A.; Dickey, E.E.; Swanson, J.W. 1976. Maximization of Soap Yield in Alkaline Pulping. Institute of Paper Chemistry, Final Report on Project 3267.
Ricard, M.; Dorris, G. 2006. Recirculation Contaminates White Water Solids. Part II: Contamination of Fines and Fillers by Extractives and Metals. *Pages* B265 – B270 *in* Preprints, 93rd Pulp and Paper Technical Association of Canada Annual Meeting, Montréal, QC, Book B.
Saltsman, W.; Kuiken, K.A. 1959. Estimation of Tall Oil in Sulphate Black Liquor. TAPPI 42(11):873–874.
Sitholé, B.B.; Sullivan, J.L.; Allen, L.H. 1992. Identification and Quantitation of Acetone Extractives of Wood and Bark by Ion Exchange and Capillary GC with a Spreadsheet Program. Holzforschung 46(5):409–416.
Sitholé, B.B.; Allen, L.H. 1994. Quantitative Analysis of Synthetic Polymers in Pulp and Paper Mill Pitch Deposits by Pyrolysis Gas Chromatography. J. Pulp Paper Sci. 20(6):J168–172.
Sitholé, B.B.; Filion, D. 2005. Determination of Silicone Defoamers in Mill Pitch Deposits. TAPPSA Jan. 2005:1–10 (http://tappsa.co.za/archive2/APPW_2004/Title2004/Determination_of_silicone_defo/determination_of_silicone_defo.html)
Soderhjelm, L.; Sagfors, P.–E. 1994. Factors Affecting the Viscosity of Kraft Black Liquor. J. Pulp Paper Sci. 20(4):106–110.
Uloth, V.; Thompson, R.; Wong, P. 2007. Black Liquor Characterization: Initial Studies. pp. 631-647 in the Proceedings of the 2007 International Chemical Recovery Conference, Quebec City, May 29– June 1, 2007.
Tikka, P.; Kosavin, K.; Laxen, T. 2002. Solving Soap and Turpentine Related Process Problems in Softwood Kraft Mills. Pulp Paper Can. 103(6):T149–T154.

Uloth, V.C.; Wong, A. 1986. The Effect of Black Liquor Soap on Evaporator Scaling Rates. Pulp Paper Can. 87(7):T267–T273.

Uloth, V.C.; Wong, A.; Wearing, J.T. 1987. Factors Affecting Tall Oil Soap Solubility in Kraft Black Liquor. *Pages* 91–103 *in* TAPPI Pulping Conference Proceedings. Washington, DC, November 1–5, 1980. TAPPI Press, Atlanta.

Uloth, V.C.; Wearing, J.T. 1988. The Use of Air Injection or Chemical Separation Aids to Increase Tall Oil Soap Skimming Efficiency. Pulp Paper Can. 89(12):T429–T435.

Uloth, V.C.; Ouchi, M.D.; Wearing, J. T.; Wong, A. 1994. The Effect of Soap Acidulation Conditions on Tall Oil Production. *Pages* 317–330 *in* TAPPI Pulping Conference Proceedings, San Diego, CA November 6–10, 2002, San Diego, CA. TAPPI Press, Atlanta.

Vakkilainen, E.K.; Pekkanen, M. J. 2002. Burning Excess Streams in Recovery Boilers. *Page* 35 (paper 13-2) *in* TAPPI Fall Technical Conference Proceedings. San Diego, CA, September 8–11, 2002. TAPPI Press, Atlanta.

Voosen, L.L. 1998. Factors Affecting Newsprint Friction and Subsequent Control of Friction with Process Changes. *Pages* 489–496 *in* (preprints) 1998 Coating/Papermakers Conf., New Orleans, LA May 4-6, 1998. TAPPI Press, Altanta, Book 1.

Young, R. 1989. Crude Tall Oil Burning at Northwood Pulp & Timber Ltd. Pulp Paper Can. 90(3):T82–T85.

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Appendix: Resin acid profiles

Figure 1. Kraft mills
Figure 2: TMP plants
Figure 3: Paper mills

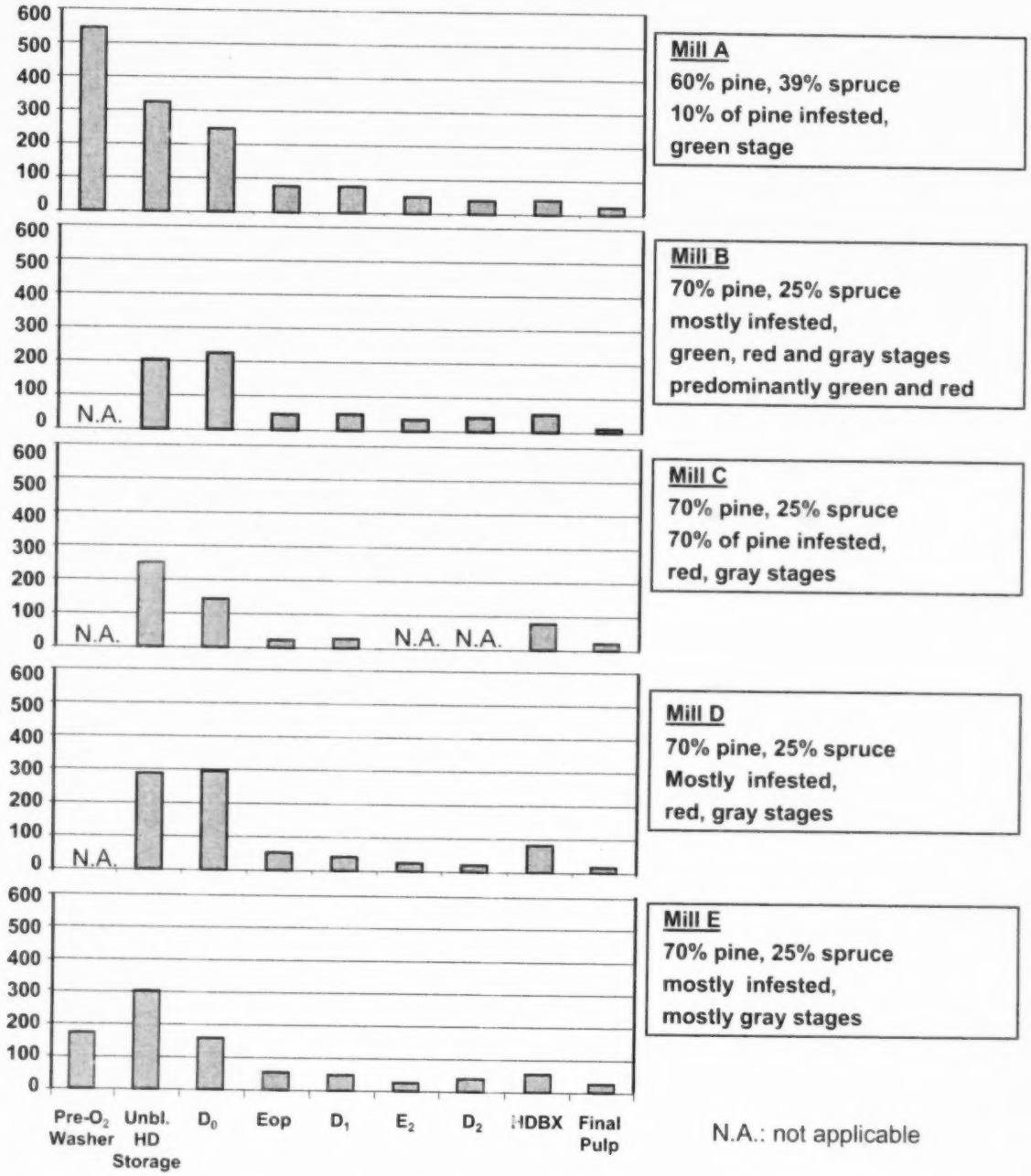

Figure 1. Concentrations of resin acids in pulps at key points along the process stream for kraft mills.

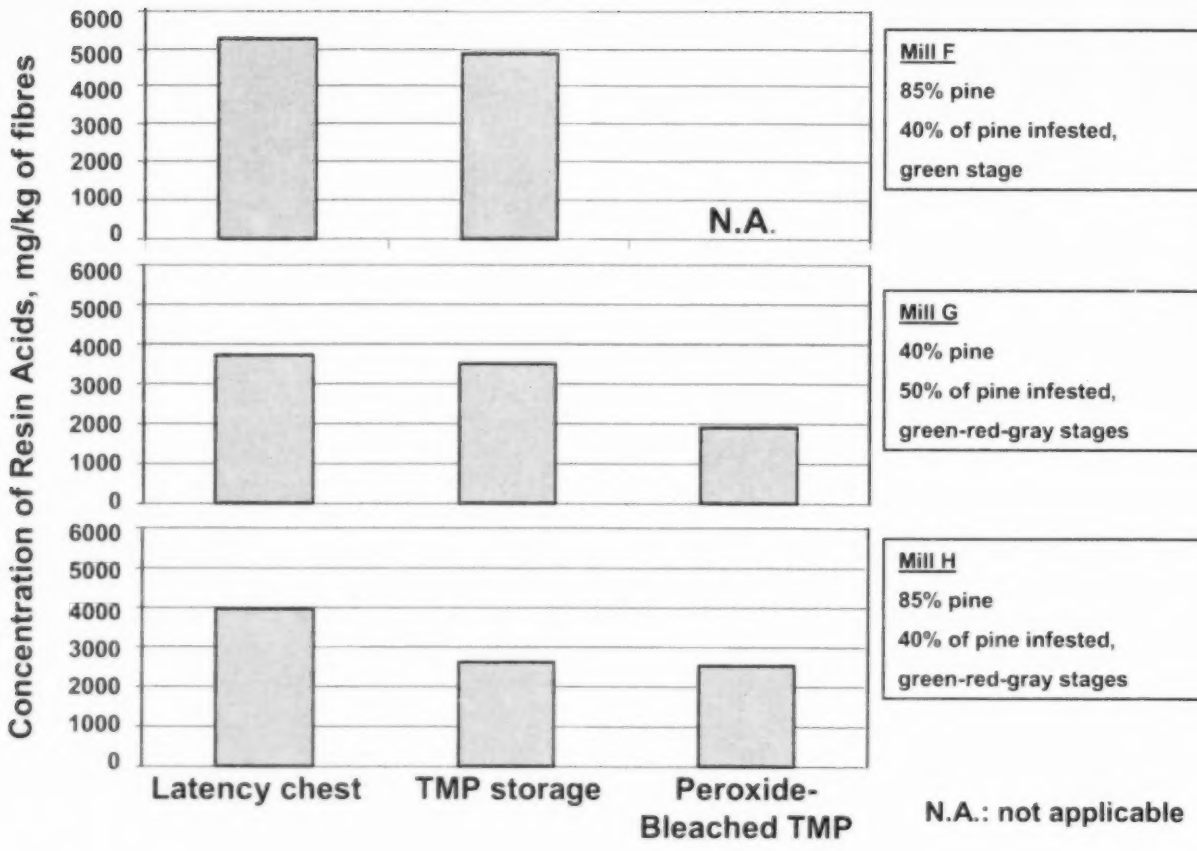

Figure 2. Concentrations of resin acids in pulps at key points along the process stream for TMP mills.

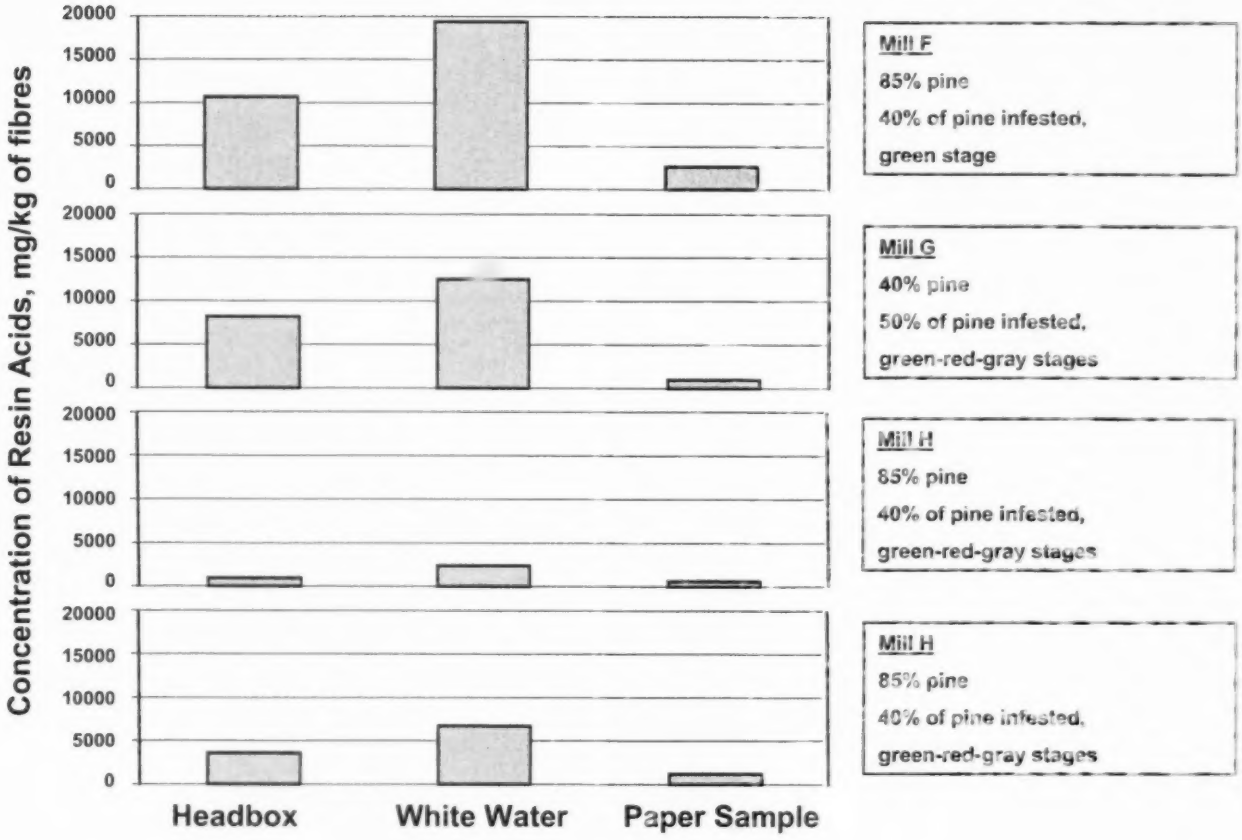

Figure 3. Concentrations of resin acids in pulps at key points along the process stream for paper mills. Mill H has several paper machines.

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